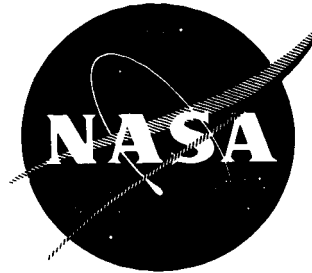


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CODE-1
CAT. 16

**CO₂ REDUCTION UNIT DESIGNED
FOR
CONTINUOUS ZERO GRAVITY OPERATION**

By
A. D. Babinsky

Prepared for
**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NASw 650**

OTS PRICE

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XEROX

MICROFILM

TRW ELECTROMECHANICAL DIVISION

THOMPSON RAMO WOOLDRIDGE INC.
23555 EUCLID AVENUE ■ CLEVELAND, OHIO 44117

594-16360

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FINAL TECHNICAL REPORT

CO₂ REDUCTION UNIT DESIGNED
FOR
CONTINUOUS ZERO GRAVITY OPERATION

by

A. D. Babinsky

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

April 18, 1964

CONTRACT NASw-650

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Chemical Rocket Fundamentals Branch
G. Morrell, Chief

TRW ELECTROMECHANICAL DIVISION
THOMPSON RAMO WOOLDRIDGE INC.
CLEVELAND, OHIO 44117

ABSTRACT

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A

A carbon dioxide reduction unit has been designed, fabricated and tested. Carbon dioxide is reduced by hydrogen to carbon and water using flat iron plates as the catalyst. Carbon and water are continuously removed from the reaction gases. Product water is electrolyzed to oxygen and hydrogen. All components have been designed for operation in a zero-gravity environment.

Tests on the one half-man capacity unit were carried out at a system pressure of 2 psig. Steady reaction rates up to 900 cc/min of reaction gases were obtained at a reactor temperature of 1200°F. Carbon was successfully removed from the reactor during operation of the system. Total accumulated test time was 40 days of operation with one continuous run of 25 days duration.

Author

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1.0 INTRODUCTION AND SUMMARY

This is the final report covering the work carried out at Thompson Ramo Wooldridge Inc. under Contract NASw-650. This contract is for the design, fabrication, and testing of a Carbon Dioxide Reduction Unit capable of operating in a zero-gravity environment. The overall unit consists of a water electrolysis unit in addition to the CO₂ reduction reactor and its associated components.

The operation of the unit may be briefly described as follows. Carbon dioxide is reduced by hydrogen over an iron catalyst in the reduction reactor, producing water and solid carbon. The carbon is continuously removed from the reactor by a filtering system. Water which is produced is removed from the reaction gases and passed into the electrolysis unit where oxygen and hydrogen are evolved as gases. The oxygen produced is available for the cabin air, while hydrogen is added to the carbon dioxide and fed into the reactor. A CO₂ concentration unit is not included in the present contract coverage. Carbon dioxide reduction capacity of the unit was designed to be 1.2 pounds per day.

Unique design features included in the present carbon dioxide reduction unit are:

1. Method of continuous carbon removal
2. Porous plate condenser-separator used for water removal
3. Water electrolysis unit design
4. Catalyst configuration.

In environmental control systems designed for use in closed cabins over extended periods, the oxygen regeneration unit is one of the most critical components yet to be developed. Long operation of an oxygen regeneration unit suitable for use in a closed system had not been demonstrated until the 25-day run on the present unit. The object

of this program was to demonstrate such operation with the capability for continuous removal of carbon from the reduction reactor. Additionally, the development of a compact and efficient water electrolysis unit was required.

Design, fabrication, and endurance testing of the CO₂ reduction unit has been completed. The reduction reactor has been operated at 150% of nominal design capacity and all other components have demonstrated satisfactory functional performance. The water electrolysis unit has been operated for 365 hours as an individual component, without being integrated with the rest of the reduction unit. While integrated with the reduction unit the cell operated satisfactorily for 16 hours.

As an extension of the present contract, it is recommended that the present CO₂ reduction unit be used as an experimental tool to determine design parameters for oxygen regeneration subsystems for actual use in space systems. Additionally, a follow on program is recommended wherein a completely integrated oxygen regeneration subsystem, including CO₂ concentration, be developed for testing at a NASA facility or at TRW.

The accumulated running time on the Reduction Unit amounted to 40 days with the two longest runs being 9 and 25 days.

2.0 DESIGN DISCUSSION

The reduction of CO₂ with H₂ (over a catalyst) to form water and deposit carbon is one of the few methods sufficiently far along in development to be integrated into an oxygen regeneration subsystem for use in early manned space stations. The reduction of CO₂ in the reduction unit may be summarized with the following equation:



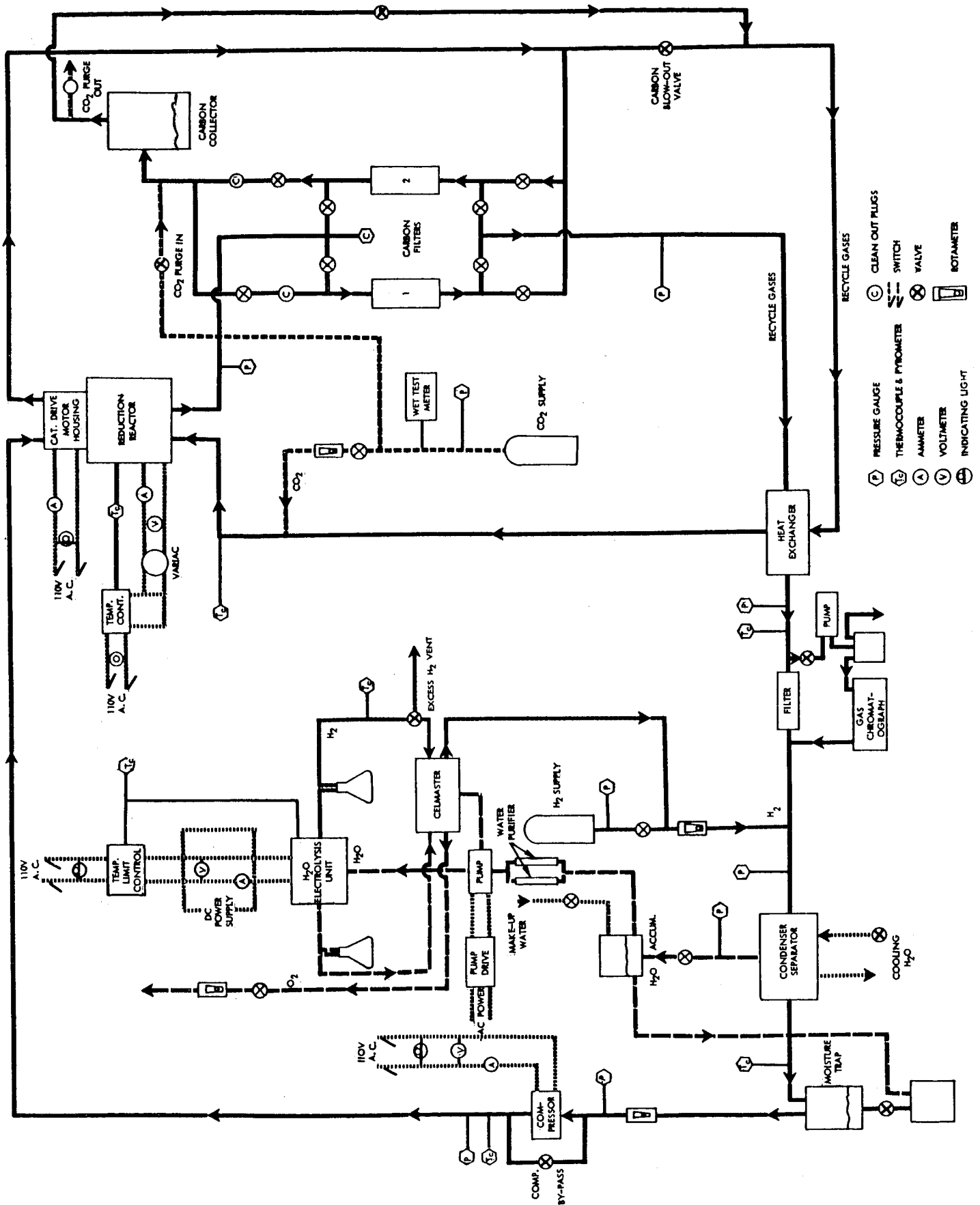
Sufficient reports covering the background and chemical kinetics of this reaction exist in the literature^{1, 2, 3, 4, 5}; a detailed discussion is therefore not warranted here.

2.1 CO₂ Reduction Unit

The CO₂ reduction unit can best be described by referring to the schematic flow diagram in Figure 2-1. The major components of the unit are the reduction reactor, carbon filters, carbon collector, heat exchanger, condenser-separator, compressor, and electrolysis unit. Carbon dioxide is supplied to the unit by bottle storage. Thermal control consists of automatic control of the reactor electrical heater (with manual override) and manual control of cooling water flow to the condenser-separator.

Bottled carbon dioxide is fed into the reduction reactor, where the reduction of carbon dioxide by hydrogen in high temperature catalyzed reactions gives the overall result indicated by the chemical reaction in equation (1). Carbon which is produced in the reactor is continuously removed from the reactor by recirculation gases, then filtered from the gases by porous stainless steel filters. As one filter approaches its capacity, the gas flow is diverted through the second filter; the first filter is then cleaned by back flow of gases through the carbon collector, causing the carbon to be deposited in the collector. Back flow is accomplished by closing filter selector valves and opening carbon blow out valves associated with the loaded filter. When these two valves have been properly positioned, the recycle gas is diverted through the carbon collector loop by closing the main carbon blow out valve on the control panel.

CO₂ REDUCTION UNIT SCHEMATIC



The recirculation gases (CH_4 , CO , CO_2 , H_2 and H_2O) after passing through the carbon filters enter the regenerative heat-exchanger and condenser-separator, where gases are cooled and the reaction water is removed. A filter is placed in the line before the condenser-separator to prevent any foreign particles from entering the pores in the condenser-separator. From the condenser-separator the recycle gases are compressed and fed through the catalyst drive motor chamber (motor cooling), then through the heat exchanger before being enriched with CO_2 . Fresh H_2 feed is supplied to the recycle gases at the condenser-separator inlet. After addition of CO_2 feed, the entire gas stream enters the reactor. Methane and CO are not produced in the reactor beyond that amount required to maintain equilibrium. Once equilibrium is established in the reactor, no additional CH_4 or CO will be formed since these gases are not removed from the system.

Water from the condenser-separator is forced into a water accumulator. Provision for make-up water is included in the accumulator. A precision piston pump meters a set amount of water through ion-exchange beds and then into the electrolysis unit. The feed rate is manually set. A pressure controller maintains the balance between the water feed pressure and the gas output pressure. Power input to the unit is manually set and adjusted to provide a constant H_2 output from the cells. To prevent damage to the electrolysis unit if dehydration should somehow occur, a temperature limit control will turn off the power supply when the pre-set temperature is reached. Since the output H_2 and O_2 contain water vapor, the hydrogen is injected into the recycle gas stream at the condenser-separator inlet so that the excess moisture is not introduced into the reactor.

Gas analysis is accomplished by a gas chromatograph just prior to hydrogen injection. This analysis determines what adjustments are necessary in the feed gas mixture ratio.

Sufficient indicating instruments are provided on the unit to monitor temperatures, pressures, flow rates, and critical voltages and currents.

A bypass line and valve on the compressor provides for flow control of the recycle gas stream.

2.2 Component Design

A layout drawing of the CO₂ reduction unit, Figure 2-2, shows the location of the major components. A discussion of the design of each of these components follows.

2.2.1 Reduction Reactor

The reduction reactor is the heart of the CO₂ reduction unit; associated with it are the major problems of the unit. These are:

1. Catalyst configuration
2. Gas confinement
3. High temperatures and materials compatibility
4. Carbon removal

Catalyst configuration must be determined first since this controls the reactor size and the basic reaction rates attainable with the reactor. Figure 2-3 presents a cutaway view of the reactor showing details of construction. Where possible, all structural pieces of the reactor were fabricated with 316-type stainless steel.

2.2.1.1 Catalyst Configuration

Figure 2-3 shows that the catalyst material required for the reduction reaction has the form of a stack of evenly-spaced disks. The disks are fabricated from low carbon steel sheets. A determination of the spacing between plates and the total plate area required to achieve satisfactory reaction rates were determined during TRW's experimental program prior to working on this contract. It was determined that a minimum spacing of 0.25 inches should be used with the flat plate configuration for

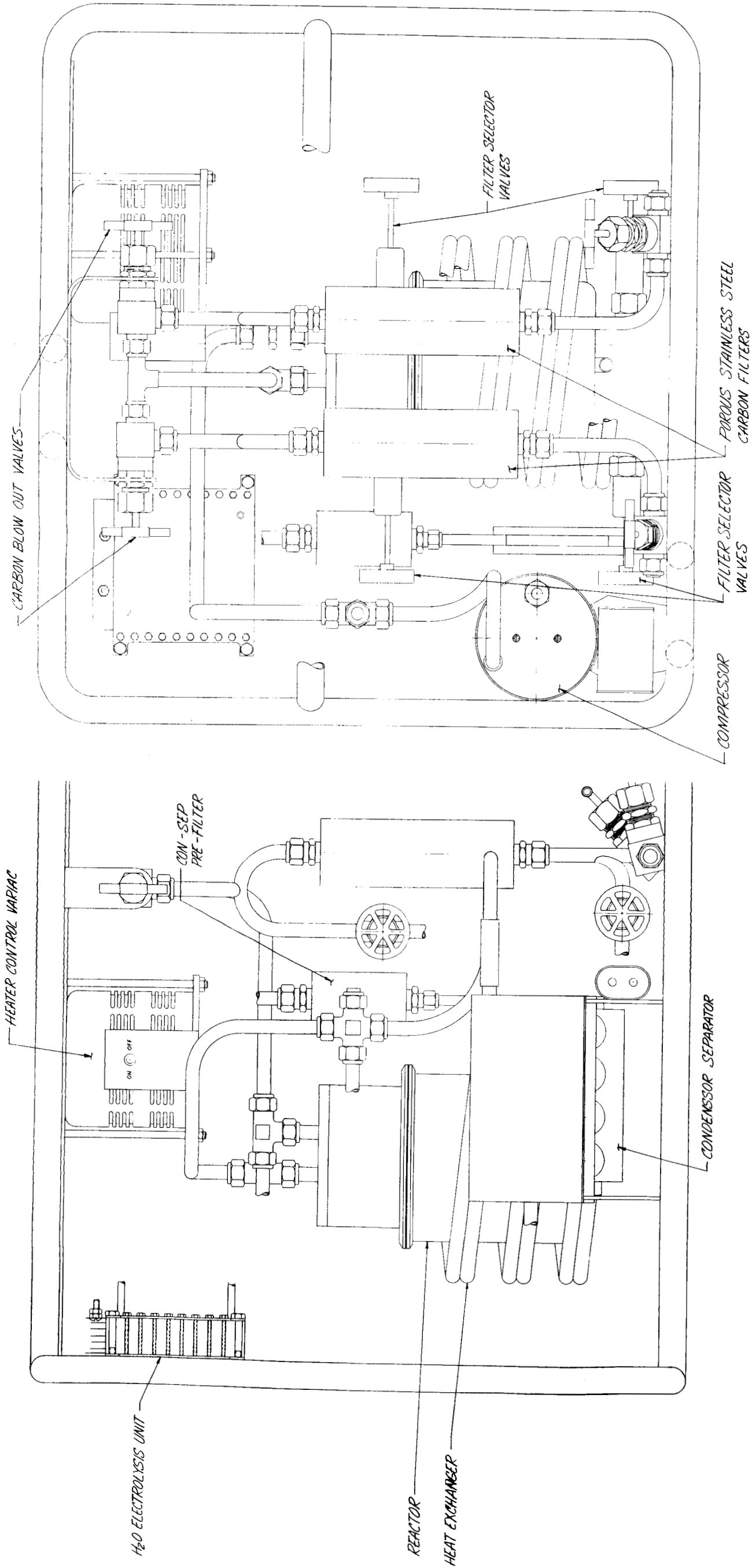
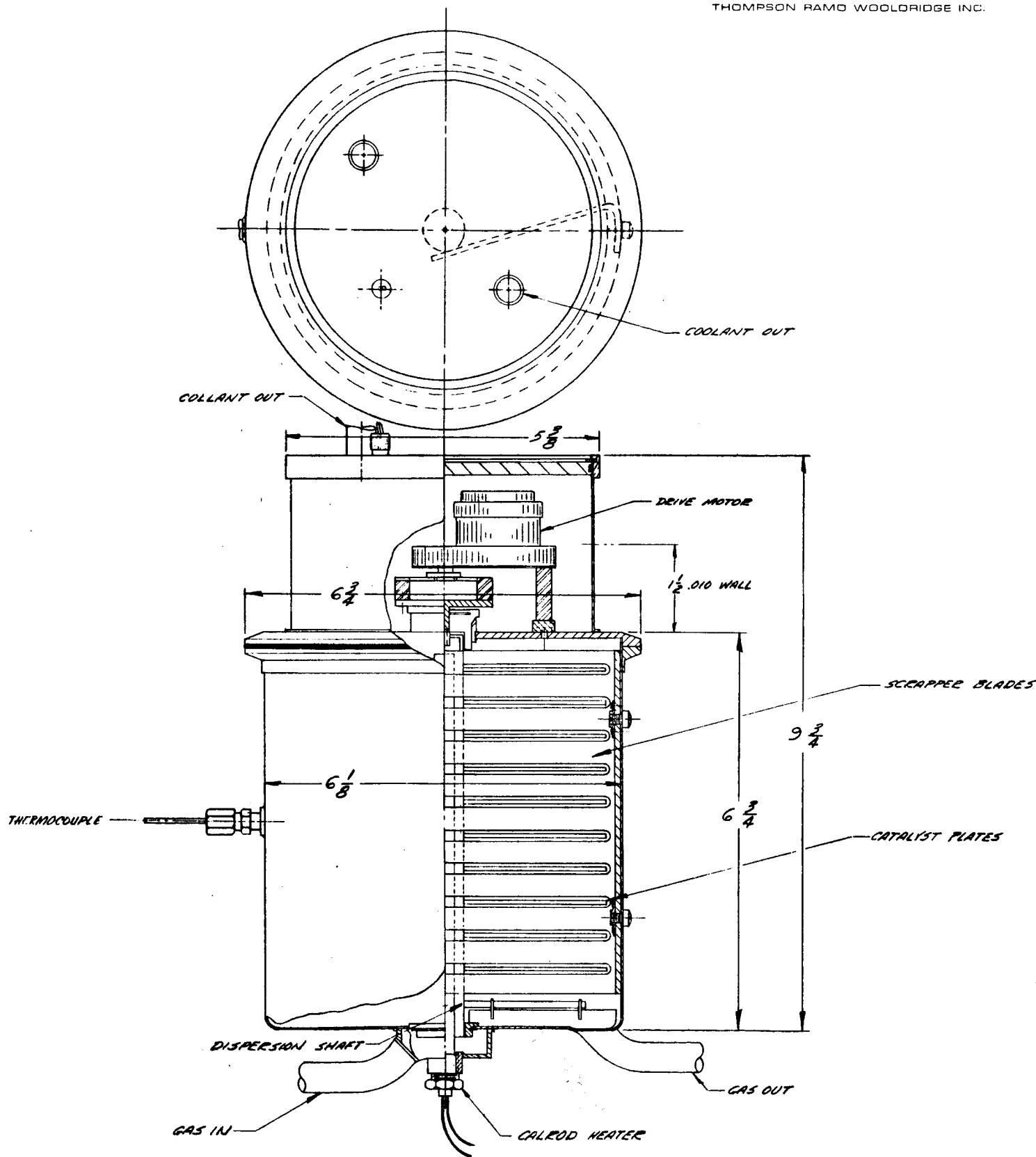


FIGURE 2-2



APPLICABLE SPECIFICATIONS	REV	DATE	BY	CHKD	APP'D	QTY	UNIT	REMARKS	LIST OF PARTS	QTY	UNIT	REMARKS
1. REACTOR LAYOUT	1	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
2. REACTOR LAYOUT	2	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
3. REACTOR LAYOUT	3	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
4. REACTOR LAYOUT	4	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
5. REACTOR LAYOUT	5	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
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79. REACTOR LAYOUT	79	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
80. REACTOR LAYOUT	80	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
81. REACTOR LAYOUT	81	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
82. REACTOR LAYOUT	82	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
83. REACTOR LAYOUT	83	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
84. REACTOR LAYOUT	84	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
85. REACTOR LAYOUT	85	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
86. REACTOR LAYOUT	86	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
87. REACTOR LAYOUT	87	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
88. REACTOR LAYOUT	88	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
89. REACTOR LAYOUT	89	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
90. REACTOR LAYOUT	90	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
91. REACTOR LAYOUT	91	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
92. REACTOR LAYOUT	92	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
93. REACTOR LAYOUT	93	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
94. REACTOR LAYOUT	94	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
95. REACTOR LAYOUT	95	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
96. REACTOR LAYOUT	96	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
97. REACTOR LAYOUT	97	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
98. REACTOR LAYOUT	98	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
99. REACTOR LAYOUT	99	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1
100. REACTOR LAYOUT	100	10-1-64	J. L. J.	J. L. J.	J. L. J.	1	1	1	1	1	1	1

FIGURE 2-3

optimum utilization of catalyst surface area. The average reaction rate per unit area was experimentally determined to be 0.5 cc/min per cm² of catalyst. Thus, for a minimum reaction rate of 600 cc of 2H₂:CO₂ mixture per minute the catalyst surface area must be at least 1200 square centimeters. However, it is known that the specific rate of reaction did vary widely, thus the minimum area requirement was doubled by using ten disks of 5.5 inch diameter with a 0.75 inch diameter center hole for mounting. The flow of reaction gases is outward from the central mounting tube. A theoretical analysis performed by TRW indicates that the cylindrical configuration as described (outward flow of reaction gases over circular catalyst plates) will give excellent reaction rates per unit area of catalyst. A spacing of 0.50 inches between plates was allowed to provide spacing for carbon removal fingers and a carbon deposit layer. Thus, disk diameter, total number disks (area required), and disk spacing determines the reactor envelope.

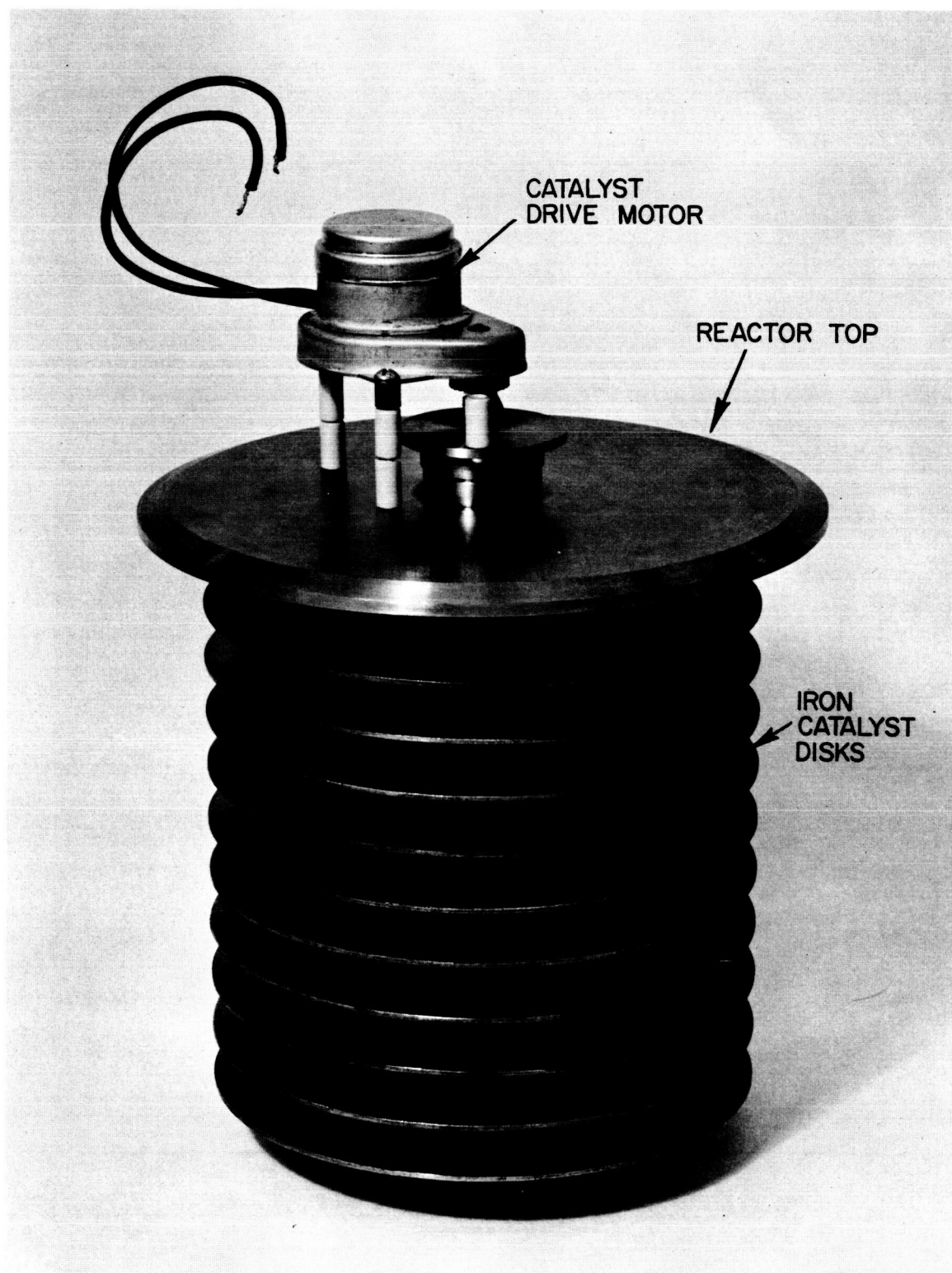
The specific reaction rate given above is for a reaction temperature of 1200°F, condenser temperature of 60°F, and a recycle flow rate of 10 liters/min.

The catalyst disks are attached to a hollow tube which is continuously rotated by a drive motor mounted on top of the reactor. A high temperature electrical heater is mounted up the center of the mounting tube. Reaction gases enter the reactor through holes in the mounting tube placed between the stacked disks. Figure 2-4 presents a photograph showing the catalyst stack and the catalyst drive motor.

With this catalyst arrangement and the reaction conditions stated, a carbon deposition to iron consumption ratio of approximately 10 is expected. Experimental results to be discussed in Section 3.0 will show the validity of the assumptions used here.

2.2.1.2 Reaction Gas Confinement

The problem of absolute confinement of hazardous reaction gases is compounded by the high operating temperature of the reactor. Two rotating bearings are required in the



CATALYST ASSEMBLY AND DRIVE MOTOR

FIGURE 2-4

present design. The bottom bearing is not a problem since a fitting was welded onto the reactor completely sealing this bearing. The bearing through the top of the reactor could not be totally enclosed since a drive motor is attached on this end of the catalyst mounting tube. Initially, it was planned to use a carbon rotating seal at this point to prevent outward flow of reaction gases. This seal, however, did not give the required performance. To overcome this problem, the drive motor and bearing assembly was completely enclosed by a welded housing.

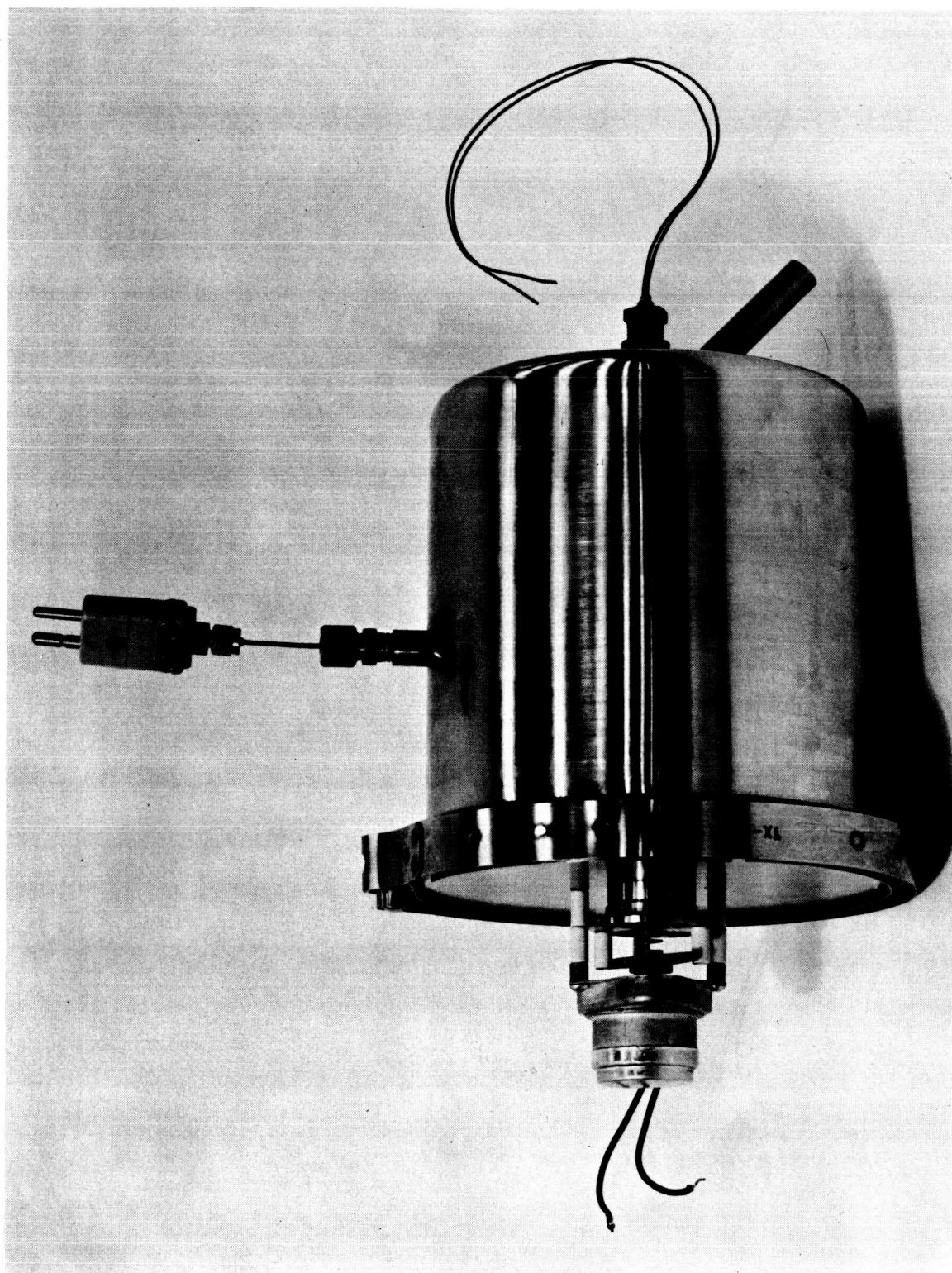
It was desired that the reactor have a top assembly which would be easily removed for inspection of the catalyst assembly. This was to be provided by a metal O-ring seal and quick release clamp arrangement. Adequate sealing was not obtained and it was decided that the reactor should be welded shut. This bead weld was opened a number of times for reactor inspection and modification. Figure 2-5 shows a view of the reactor incorporating the original design features.

Diffusion of hydrogen through the reactor vessel walls was calculated to be approximately 0.2 cc per hour for the oxidized stainless wall. Hydrogen diffusion was therefore not deemed to be a problem.

2.2.1.3 Thermal Considerations

The reduction reaction (equation (1)) is an exothermic process. However, the energy liberated by the reaction is less than the energy lost by cooling and reaction gases prior to water removal and by losses through the thermal insulation and along the metal tubing which connects the reactor to the rest of the system. The net energy deficiency, considering the worst possible conditions was calculated to be approximately 180 watts. These conditions are:*

*Higher electrical requirements during experimental testing, indicate that thermal energy losses through the insulation and losses by conduction were underestimated.



REDUCTION REACTOR - INITIAL DESIGN

1. Recycle Ratio - 30 (moles recycle gases/moles feed gases)
2. Temperature of Gases Entering Reactor - 600°F
3. Insulation Layer Thickness - 2 inches ($K = 0.55$)
4. Energy Loss by Conduction Equal to 25% of Losses Through Insulation

This energy deficiency will decrease to 75 watts if the recycle ratio is decreased to 10, inlet gas temperature increased to 850°F, and insulation thickness increased to 3 inches.

An electrical heater having a capacity of 400 watts is provided to reduce the time required to bring the reduction unit up to reaction temperature. Figure 2-3 shows that the heater, enclosed in an incoloy sheath, is mounted in the center of the rotating catalyst assembly. A maximum sheath temperature of 1750°F can be tolerated by the heater. A manually controlled variac controls heater power, while an Assembly Products Inc. "Temp-Tendor" and thermocouple controls power "on-off" to the variac for temperature limit control.

Thermal insulation used on the reactor was "J-M" Thermoflex and "J-M" Micro-Fibers Felt Type E. This material has a K value of approximately 0.55 at a mean temperature of 700°F.

The enclosure on top of the reactor to prevent leakage of gases through the rotating seal caused a severe thermal problem for the catalyst drive motor. Heat transfer to the motor chamber is minimized by placing layers of insulating material between the motor and hot reactor surfaces. A thin walled section is machined on the enclosure case adjacent to the reactor top to reduce heat transfer up the housing sidewall.

The motor mounts are heat-treated lava. Cool reaction gases are passed through the housing and over the motor to maintain a suitable operating temperature. When the reactor temperature is 1200°F, the motor chamber is approximately 120°F.

Figure 2-6 shows the modified reactor with motor enclosure after preliminary testing. The difference in oxide coating thickness along the housing wall gives an indication of the temperature along the housing wall.

2.2.1.4 Carbon Removal

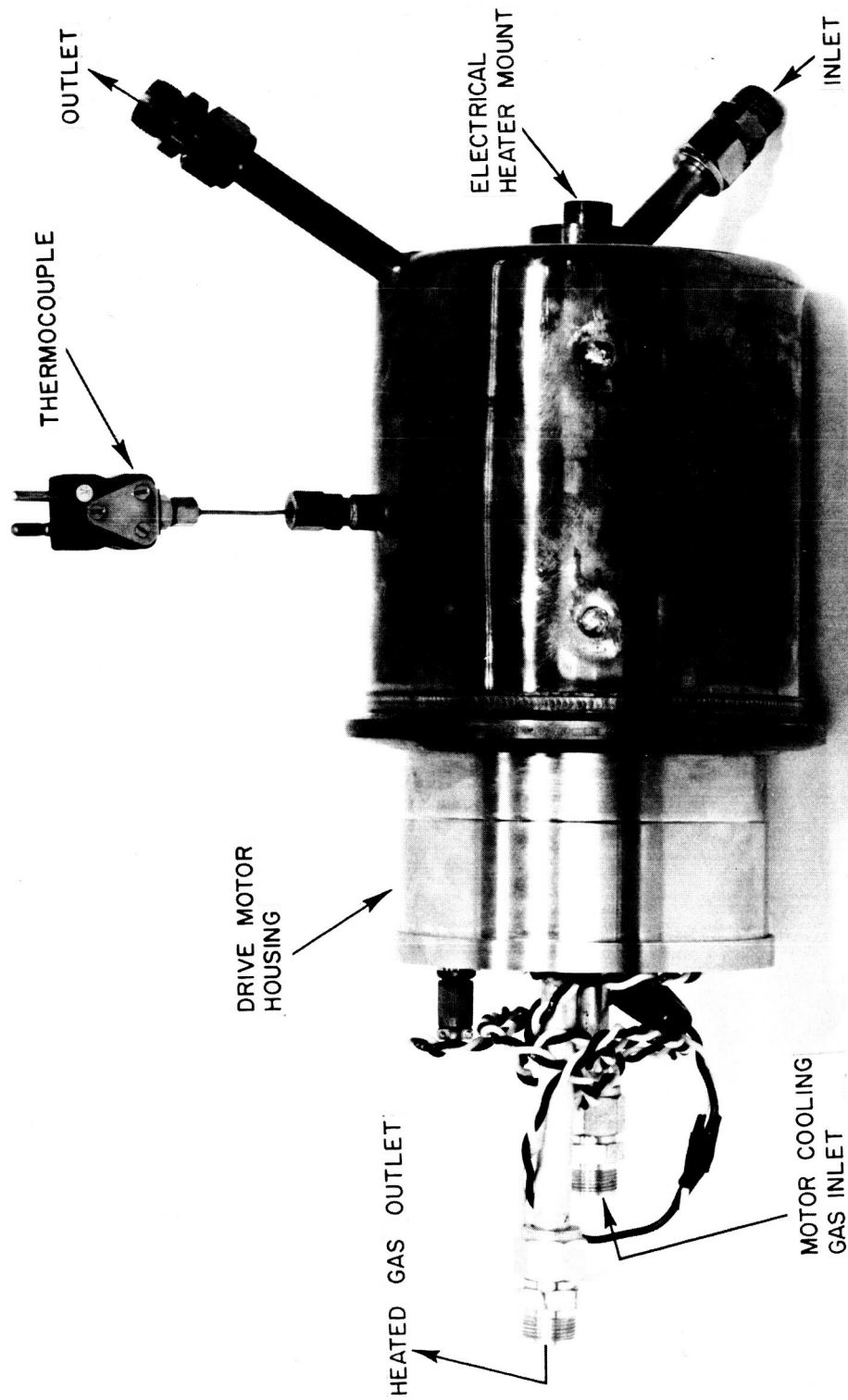
Continuous carbon removal is required if a practical reduction unit is to be developed. The method adopted in the present unit depends on easily-achieved mechanical processes. Carbon is deposited on the slowly rotating catalytic disks, which are kept free of thick carbon deposits by rotation past a bank of carbon removal fingers. The carbon which is removed from the disks is carried from the reactor by the normal gas flow over the disks. This stream of gases and carbon particles passes through a porous stainless steel filter where the carbon is removed.

Since carbon buildup can be tolerated on the catalyst surfaces, only the loose carbon above the surface must be removed from the disk. In this mode of operation, the carbon removers do not actually have to touch the surface of the moving disks. This eliminates the problem of wear. Figure 2-7 shows an interior view of the reactor with the carbon removal fingers in place.

2.2.2 Heat Exchanger

The heat exchanger for the CO_2 reduction unit is required in order to recover the thermal energy of the gases in the recycle stream which must be removed in order to condense the reactant product water. The driving force for the exchanger is the sensible entropy difference generated by energy removal in the condenser-separator which is in the line between the hot and cold loops of the heat exchanger.

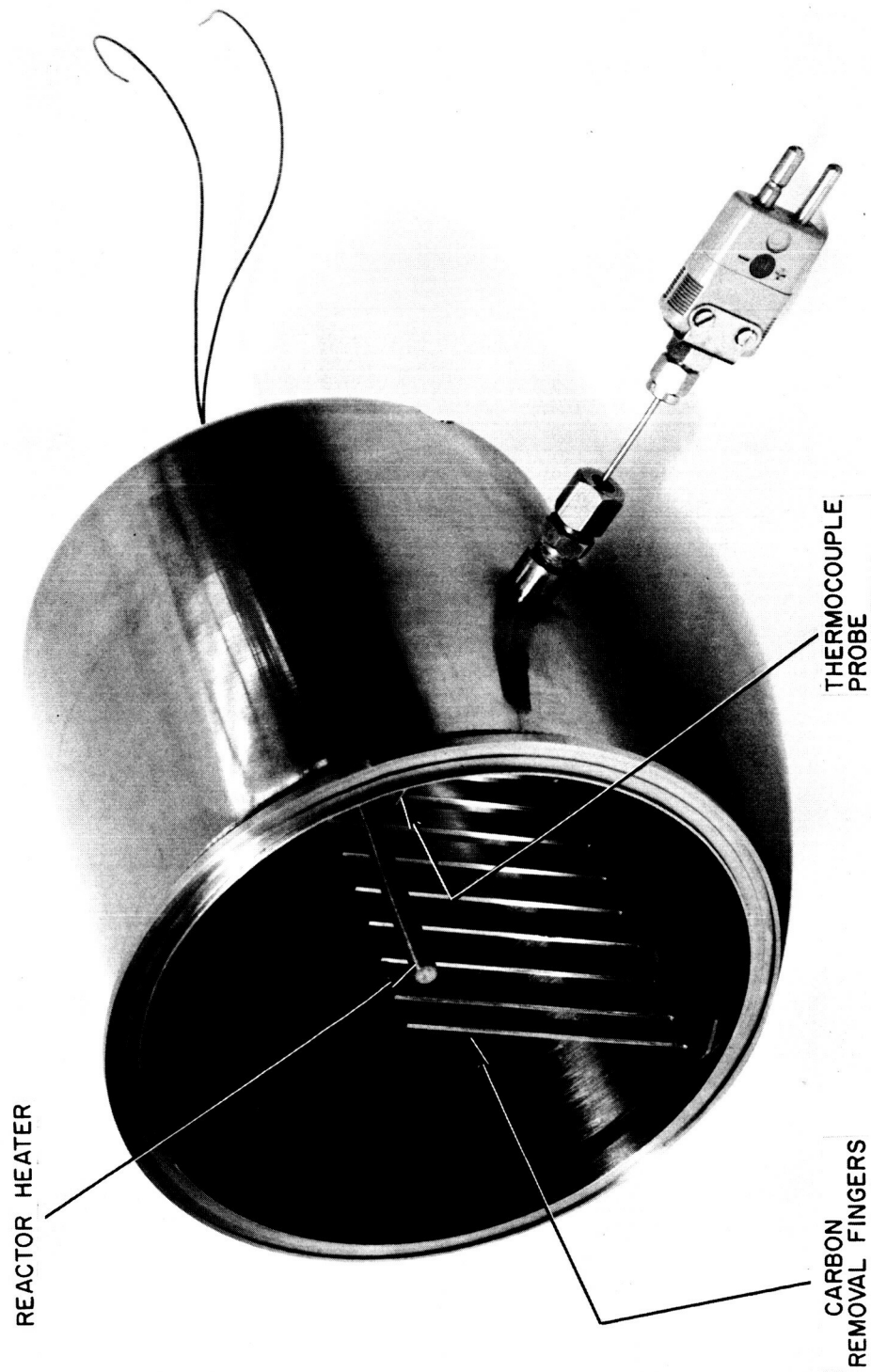
A counterflow type of heat exchanger is used. Geometrically, this consists of two side-by-side tubes, carrying the hot and cold flows. The energy flux occurs across the common junction of these tubes. The most efficient design would result if tubes



MODIFIED REDUCTION REACTOR - AFTER PRELIMINARY TESTING

884C

FIGURE 2-6



of square cross section were used with the major thermal energy transport occurring across a plane surface. However, because of fabrication ease, tubes of circular cross section were used. An empirical law indicates that an exchanger built of circular tubes will have 85% of the effectiveness of a similar one built of tubes with square cross sectional shape. Using 0.5" copper tubing brazed together with brass it was calculated that a heat exchanger 4.0 feet long would be required. Preliminary testing indicated that this length was not adequate. Using this preliminary test data, the new length was calculated to be approximately 6.0 feet. Testing under simulated operating conditions indicated an effectiveness of 0.955, which was satisfactory.

2.2.3 Carbon Filters

Two types of filters are required to completely remove the product carbon from the reduction process stream: a high temperature regenerable filter and a large carbon collection chamber and filter (low temperature). The carbon collection chamber has sufficient capacity for three weeks continuous operation. The bulk carbon can be removed from this container while isolated from the remainder of the system. This low temperature filter chamber is fabricated with clear acrylic plastic with a 0.5 inch thick felt pad for the filter element.

The high temperature carbon filters are placed in the system between the reactor and heat exchanger. These filters are fabricated of two concentric cylinders. The inner cylinder is a porous stainless steel with a solid disk welded to one end, while the outer cylinder is solid 316 stainless steel. Figure 2-8 shows a cross-sectional layout of the filter. The porous stainless steel filter element is a Pall Corporation element part No. C-12-6, Grade G. Mean pore size is 10 microns, giving absolute filtration of particles 1.8 microns or larger from gas streams. For 1/16" thick material, the pressure drop for air flow at 0.5 CFM is 0.08 psi when the filter is empty. Pressure drop through a filter 80% filled with carbon is expected to be 0.3 psi. These numbers were determined by actual testing of gas flow through beds of carbon generated by

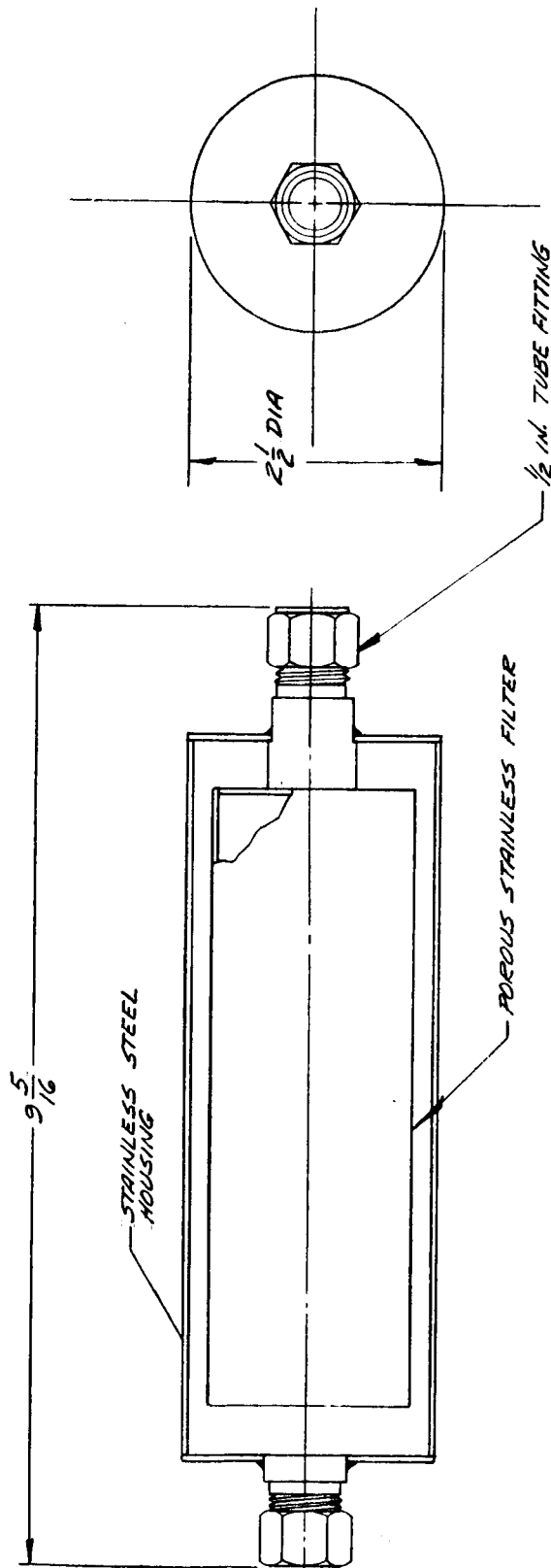
[illegible]

FIGURE 2-8

various TRW CO₂ reduction reactors. It was originally intended that each filter would be filled with carbon and emptied by back flow into the carbon collector once a day. However, the amount of carbon required to fill a filter to this capacity is too difficult to force through valves and pipes to the carbon collector. A one-hour cycle can readily be handled.

2.2.4 Condenser-Separator

The condenser-separator unit performs the function of removing the water from the recirculating gas stream and providing dry gas to be fed back into the reactor. To accomplish this end it is necessary that additional sensible heat be removed from the gas stream over and above that removed in the regenerative heat exchanger. The temperature level must be reduced to that corresponding to the saturation temperature of the gases; then the latent heat corresponding to the required amount of water to be removed must also be removed from the stream.

Figure 2-9 shows an exploded view of the condenser-separator. Water condenses on a cold plate as the recirculation gas flows through the unit. The cold plate upon which the condensation occurs is a porous plate of sintered nickel. The plate has a 10-20% porosity and a pore size of approximately 1 micron. The H₂O upon condensing on the porous surface is immediately drawn through the pores by means of the capillary forces. The water collects in the passages machined on the surface of the copper back-up plate.

The size of the condenser-separator is determined by heat transfer requirements through the raised stubs on the copper back-up plate. More than adequate area is available for flow of condensed water through the pores.

The porous nickel plate used in this condenser-separator can resist a gas pressure in excess of 6 psid. Previous to use of the nickel plates, porous stainless steel backed by an asbestos layer was used. The asbestos is capable of resisting gas pressures up to 15 psi. Because of the better qualities of the nickel plates, asbestos is no longer required.

CONDENSER-SEPARATOR ASSEMBLY

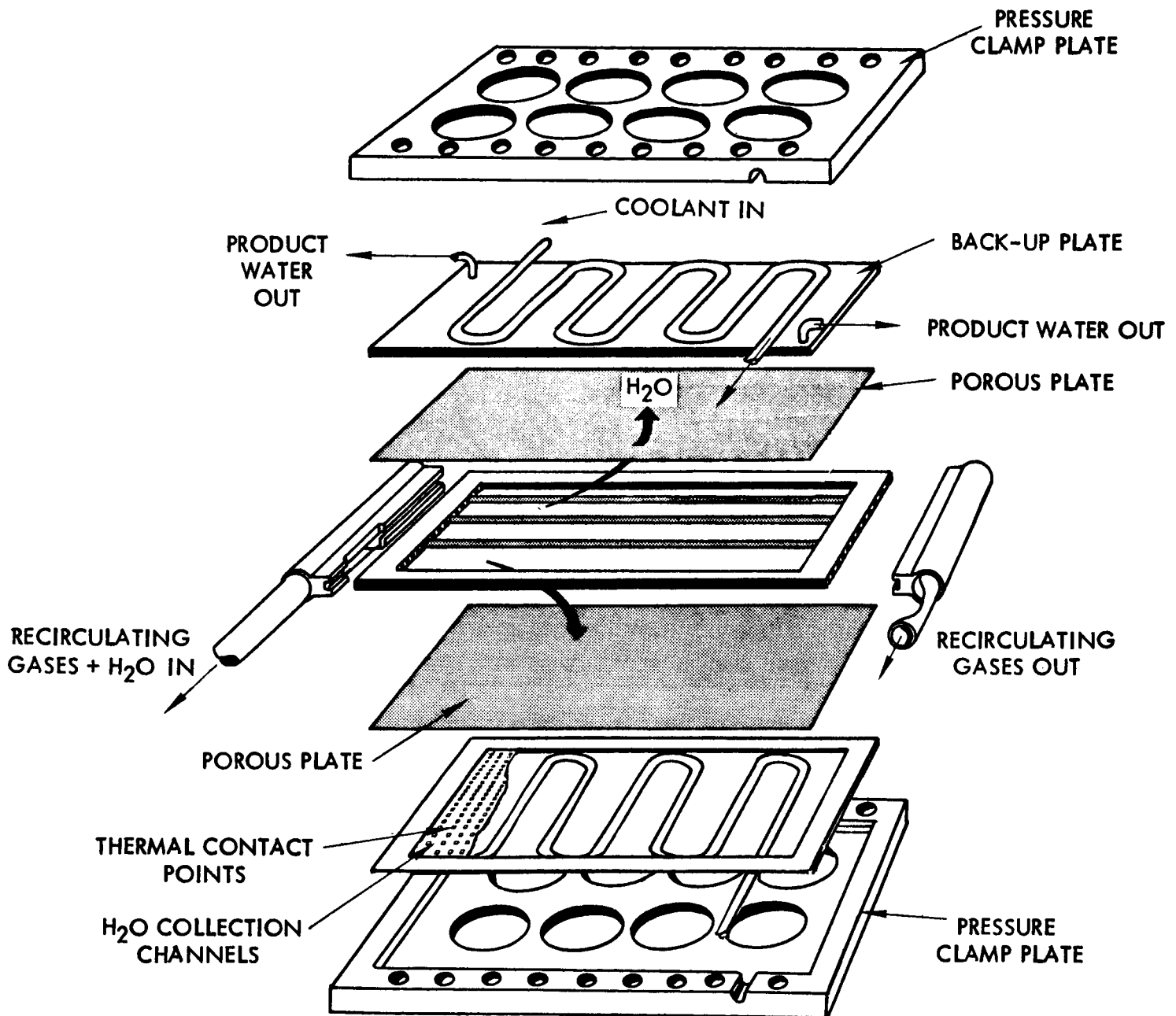


FIGURE 2-9

Cooling is provided by cold water flowing through the cooling coils brazed on the back of the back-up plates. Coolant temperature was maintained at about 45°F in order to obtain a recycle outlet temperature of 50°F. Cooling water flow rate was manually controlled.

This type of condenser-separator produces very slight pressure drops in the gas flow through the unit, while providing recovered water at a positive pressure.

Pressure plates are used to hold the pieces together, with RTV silicone rubber used as a sealant and bond between the porous surfaces, the main frame, and the copper back-up plates.

2.2.5 Compressor

Blower requirements for the CO₂ reduction unit are for relatively low flow rates coupled with a significant pressure rise through the blower. The design point calls for 0.5 CFM at a pressure drop through the system of approximately 2.0 psi.

Small variations in pressure are observed due to collection of carbon in the filter chambers.

These gas flow requirements are satisfied by a carbon vane compressor driven by a constant speed motor. Both motor and compressor are sealed in a single aluminum housing to prevent leakage of gases from the compressor shaft seals. Figure 2-10 presents a layout drawing of this compressor. Recycle gases from the condenser-separator (50°F) pass over the motor into the compressor inlet. Compressor outlet temperature was normally 110°F. Motor cooling is accomplished by recycle gas flow through the blower unit and conduction through the aluminum housing to the unit framework.

The motor used is an Air Marine 60-cycle Induction motor, Model No. B 1121-84 using 98 watts electrical power while running at 3300 rpm. The compressor is a Gast Model No. 1030 oil-less carbon vane air compressor.



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2.2.6 Electrolysis Unit

The design and construction of an efficient electrolysis unit for gravity free environment depends on the use of the best possible electrodes and on a suitable feeding system for water. The electrode material used in this model is a product of American Cyanamid. It consists of a 100-mesh nickel screen coated with platinum black. Teflon dispersion is used as a binder.

With the electrode material fixed, the next step was to choose a feeding wick. Because of the presence of KOH, an inert material is a necessity. For the conditions of cell operation, polypropylene is the best readily available material. While it does not wet easily, once it is wet it acts as a good wick. The material used in the cell is a woven filter cloth with a nap on one side. It was selected not only because of its chemical inertness but also because of its ability to transport water.

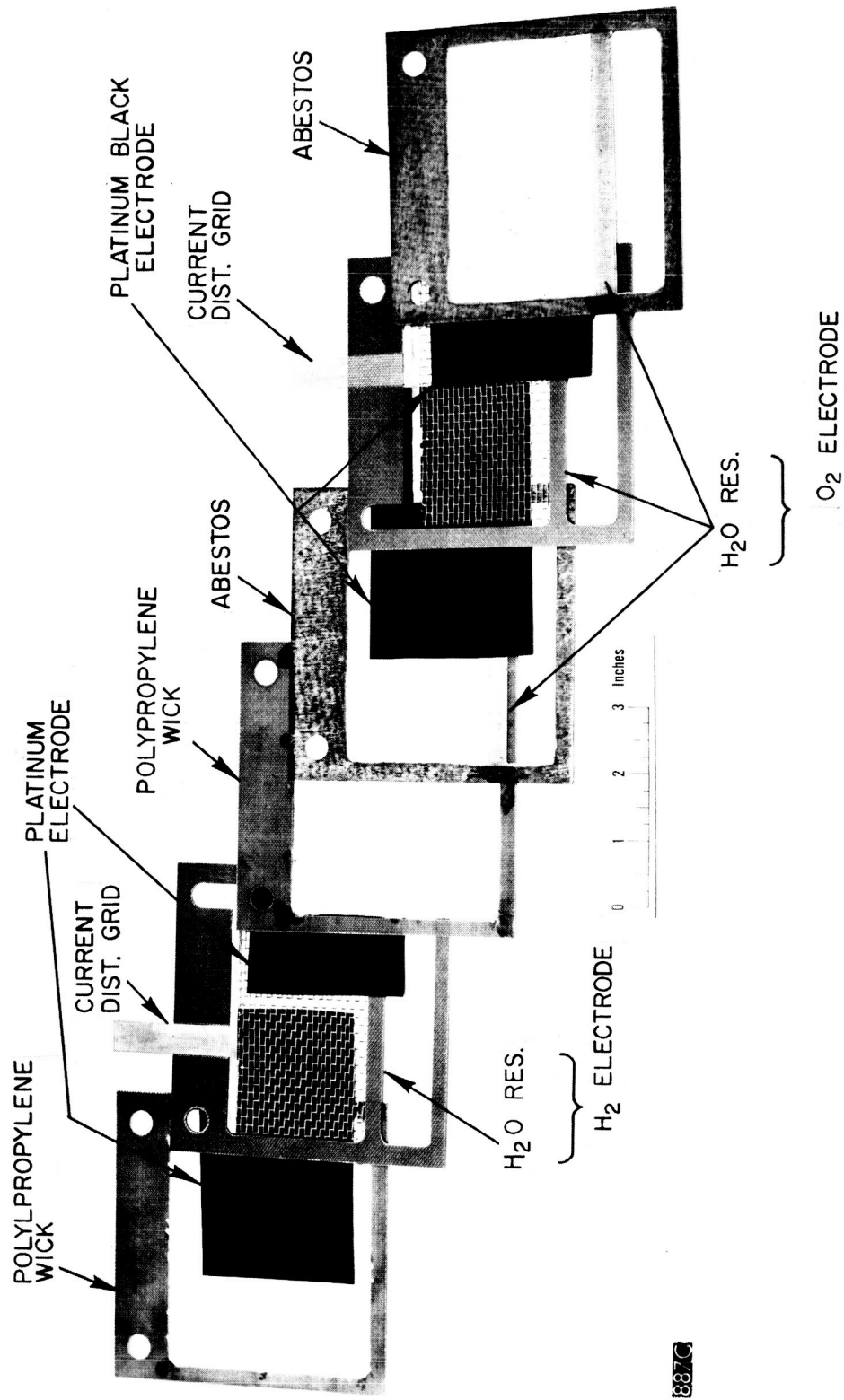
The transport properties of the various wicking materials were determined by placing them between two acrylic plates which were marked at 1-, 2-, and 3-inch intervals. The rate at which KOH as water solution was transported from bottom to top determined the material to be used. However, since the rate slows down as the height increases, the electrolysis cell was designed to minimize the maximum height from the reservoir to the top of the cell. This will aid the operation of the cell at 1 g. At zero g this will no longer apply.

An addition to the wick and electrodes, an asbestos diaphragm is used. This prevents the mixing of the gases. The particular material used in the construction of the first two units is a special 15-mil electrolysis cell material that withstands up to 15 psi differential gas pressure when wet.

The power requirements for the cell are those required to produce enough oxygen to satisfy half the requirements of one man. The oxygen required by one man is produced by a current of 100-125 amperes, depending on the specified oxygen requirements. For a conservative design, the 125 ampere figure was chosen, so the cell is designed for 65 amperes with a current density of 100 ASF. The result is a cell which could operate at much higher currents if necessary. Because of the type of cell geometry, this conservative design requires very little extra volume,

The materials of construction, in addition to those already mentioned, are epoxy-glass fiber board, monel screening, and copper. All of the metal items were plated with a nickel flash after fabrication to protect the copper and monel from the KOH. Figure 2-11 shows the parts that are assembled to form individual cells of the unit. These parts are bonded to each other with an epoxy cement which is alkali resistant. The entire assembly of cells is bonded to two end plates. One of these is a piece of epoxy-glass fiber board, the other is an assembly of tubes silver brazed to a copper sheet and then nickel plated. This metal plate was then covered with an insulating epoxy-glass fiber board. The entire assembly is held between two bowed steel plates. When the side bolts are tightened until the plates are flat, there is enough pressure against the assembly to allow safe operation of the unit at low pressures. The total assembly is then potted with epoxy to give added strength. Figure 2-12 is a drawing of the completed assembly.

The internal construction of the electrolysis cell is such that the pressures of the H_2 gas and water feed must be equal. Thus a method of increasing feed water pressure and output gas pressure must be used to prevent electrolyte blow out or feed water blow back. Water feed into the electrolysis unit was accomplished by a Harvard Apparatus Co., Lambda Pump capable of accurate control of flow rates. The flow rate is capable of being controlled in steps of 0.006 cc per minute. The approximate flow rate required is 0.366 cc per minute. Control is manual.



H₂O ELECTROLYSIS CELL COMPONENTS

ELECTROLYSIS UNIT

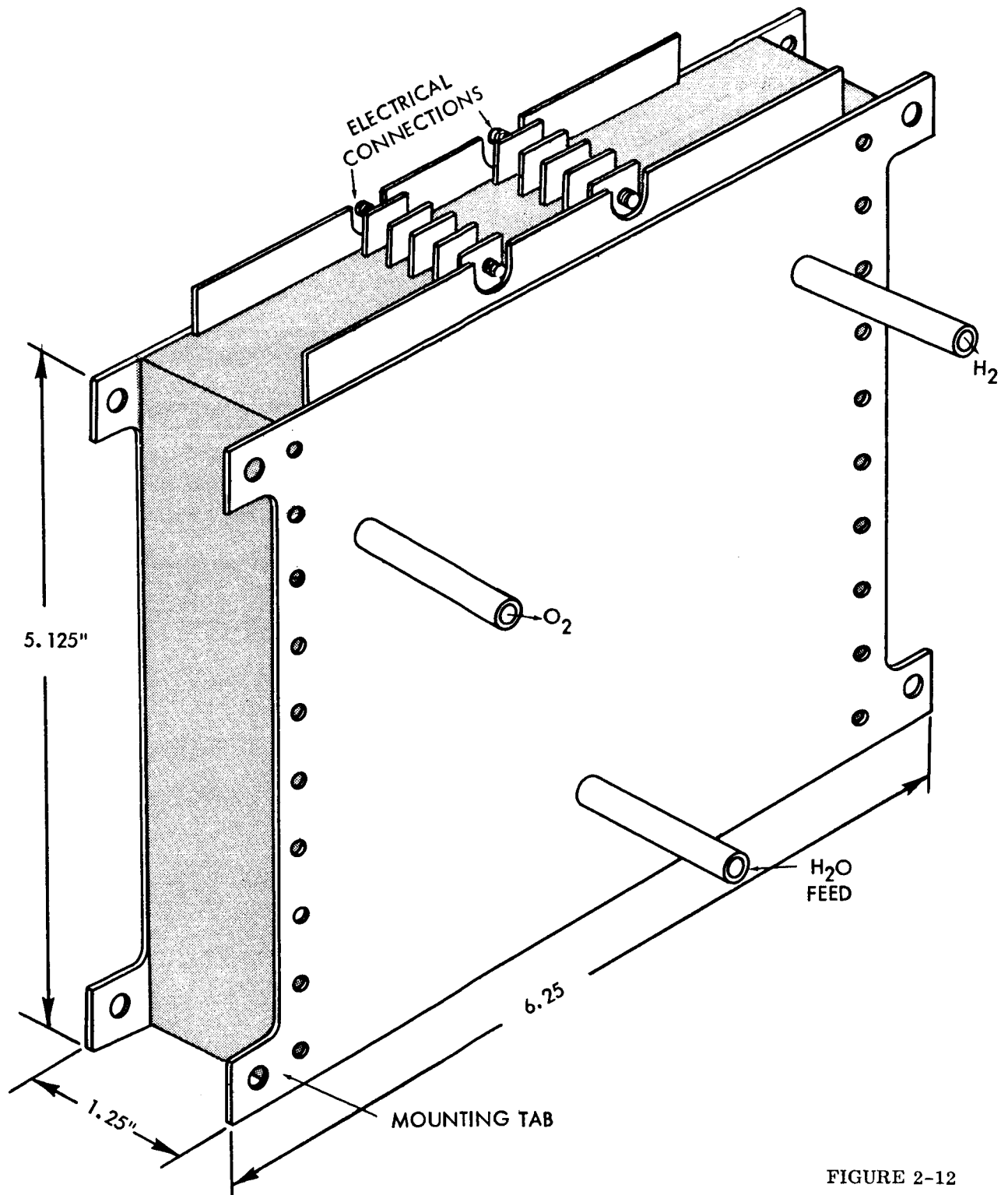


FIGURE 2-12

Pressure balance between pump and gas output was maintained by a Honeywell "Cellmaster" pressure control in initial cell testing. These tests have shown that with a "Cellmaster" controlling the output of the electrolysis unit, the pressure difference between feed water, O₂ gas, and H₂ gas was maintained at about 1.0 inches of H₂O.

Although the gas pressures were properly balanced by the "Cellmaster", the internal pressure of the electrolysis unit continued to rise to a point where rupture of the unit could occur. In this application, the "Cellmaster" was thus not able to properly control the unit pressures. Modifications in the electrolysis unit construction (3rd unit fabricated) resulted in cell performance such that a pressure controller such as the "Cellmaster" was not necessary.

The first two electrolysis units which were fabricated could only maintain a few inches pressure differential across the asbestos diaphragm rather than the expected pressure differentials (~ 10 psi). This performance could have resulted from a number of flaws in construction. These are:

1. Weakening of asbestos pore structure by impregnating asbestos with epoxy to form sealing border.
2. Asbestos with structural flaws.
3. Improper bonding of fiberboard end piece to metal end plate.
4. Improper bonding around gas manifold at top of cell assemblies.

A third electrolysis unit was fabricated in which the asbestos diaphragm design was changed and the metal end plate (tube attachment plate) was replaced by a plastic end plate with metal tubing attached to the plastic plate. The original asbestos was replaced by 30 mil asbestos "Fuel Cell Board."

Prior to cell assembly the asbestos was not impregnated with epoxy to form a border seal. An additional change was that the water reservoir cutout was reduced to a 1/4" punched hole at the location of the water inlet tube. The entire electrolysis unit was stacked without epoxy cement (after hydrogen electrodes were assembled) and compressed at the edges by clamping. The entire unit was then potted with KOH resistant epoxy compound. This assembly technique thus provided a wetted asbestos seal between oxygen and hydrogen chambers rather than possible faulty epoxy to plastic sealing.

The electrolysis unit was successfully tested to a 3.5 psi gas pressure differential across the wetted asbestos diaphragm. Higher pressure differential pressures were not used. Since this unit was able to withstand this high pressure differential, it could be operated without a close balance between the O₂ and H₂ outlet pressures.

2.2.7 Miscellaneous Components

A number of minor components are extremely important to proper operation of the unit. Without these components, failure of the unit could result after a relatively short period of operation.

Carbon Filter Selector Valves

Early in the unit test program, it was determined that special valves were required for use as the filter inlet selector valves. These valves must operate at high temperature (1200°F) and offer no obstruction to the flow of carbon through the valve. The required valves were not commercially available. Under a TRW funded program, high-temperature carbon plug valves were developed. These valves performed well with virtually no external leakage. Internal leakage was extremely small and entirely acceptable.

Condenser-Separator Pre-Filter

Just prior to the condenser-separator is a small filter of fiber glass filling to remove any particulate matter which might enter the pores in the condenser-separator, and thus clog the plates and prevent the passage of water. The amount of foreign matter which enters this filter during normal operation is very small, so that filter cleaning was not required during the total period of operation.

Moisture Trap

A moisture trap placed in the recycle flow line at the condenser-separator outlet removes the small amount of water which is not removed in the separator. This prevents slugs of water from being drawn out of the flow line and into the compressor. Trapped water is removed by a valve in the bottom of the trap.

Water Accumulator

Output water is collected in a small accumulator from which the Lambda Pump will draw water for the electrolysis unit.

Gas Analysis Equipment

Gas composition analysis is performed using a Beckman GC-1 Gas Chromatograph with molecular sieve and silica gel columns.

Ion Exchange Beds

Product water from the condenser-separator must be passed through a mixed bed of ion exchange resins to remove dissolved CO_2 and other impurities which would poison the alkaline electrolyte electrolysis unit causing severe performance degradation.

3.0 TESTING PROGRAM

3.1 Component Testing

Testing of components prior to assembly into the CO₂ reduction unit was necessary in order to insure adequacy of component design and to check purchased components for specified performance. Upon completion of the unit testing and prior to initiation of the endurance run, it was necessary to determine what modifications were required for proper operation and what operating characteristics would yield optimum performance.

All components were pressure checked and subjected to the thermal and gaseous environment expected during actual operation. Additionally, the following functional tests were performed.

3.1.1 Reactor

The most important functional test for the reactor was the determination of the reaction rate for the catalyst configuration in the reactor. A sufficiently high rate must be obtained or the reactor is useless in that configuration. Figure 3-1 presents a plot of the reaction rate and reactor temperature as a function of running time. The present unit was designed for a nominal reaction rate of 600 cc/min of 2H₂:CO₂ gas mixture at a reactor temperature of 1200°F. Figure 3-1 shows that a steady rate of 900 cc/min was achieved at 1100°F reactor temperature.

It should be noted that the condenser temperature was approximately 72°F or 20°F higher than the planned condensing temperature. A lower condensing temperature favors a higher reaction rate. Recycle gas flow rate was 13 liters/min. Recycle gas flow rate for the planned testing was approximately 16 liters/min. Higher recycle gas flow rates favor higher reaction rates. It was thus shown by this preliminary testing that the reactor is designed so that adequate performance could be expected.

RECYCLE GAS COMPOSITION

N ₂	-	12%
CH ₄	-	4.5%
CO	-	23.0%
CO ₂	-	24.0%
H ₂	-	36.5%

PRELIMINARY REACTOR TEST
 RECYCLE PARTS - 13 LITER/MIN
 CONDENSER TEMPERATURE - 74°F

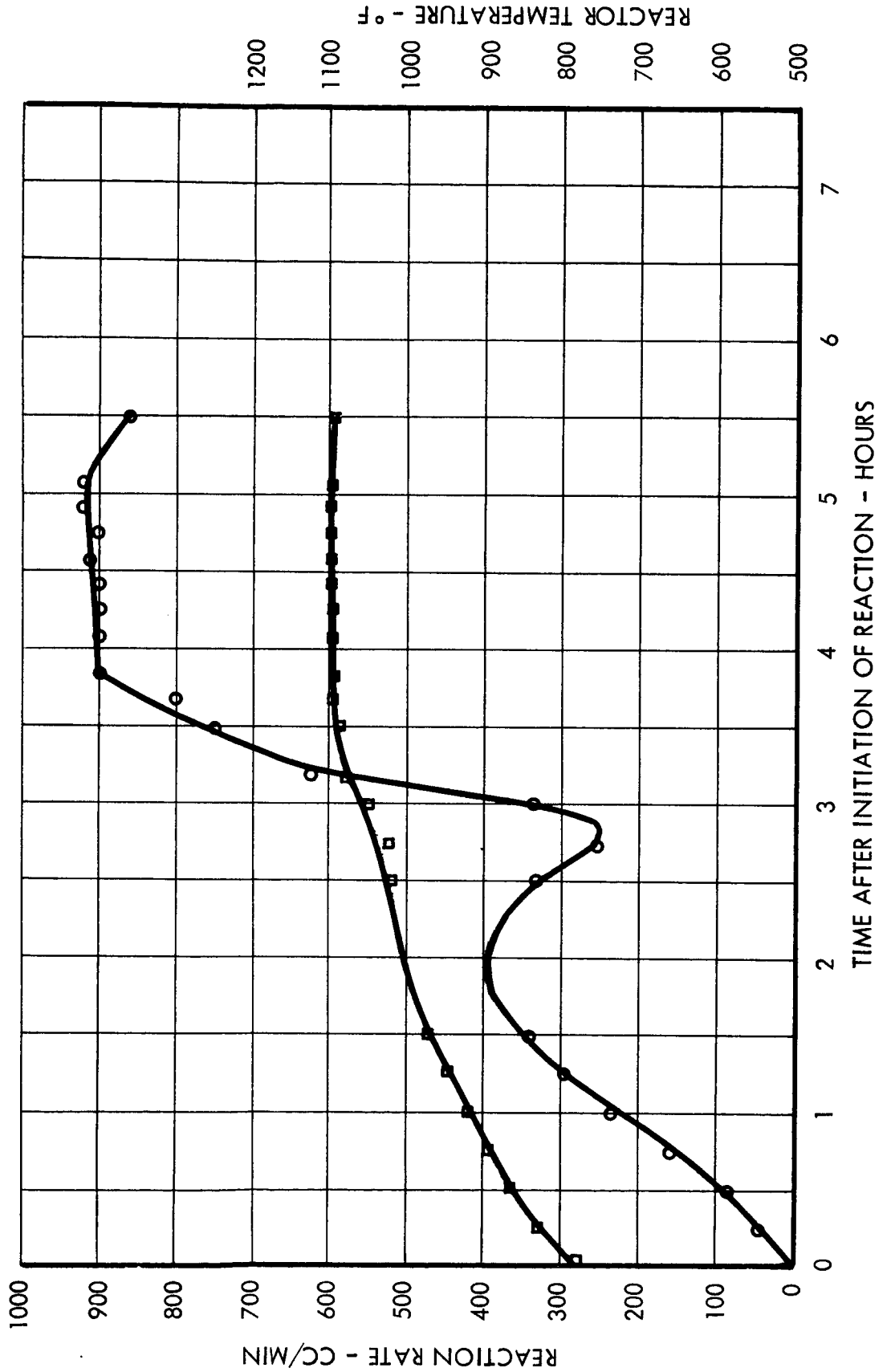


FIGURE 3-1

During preliminary reactor testing, two types of electrical cartridge heaters failed below their rated operating temperatures. A source was located for heaters capable of operating in a 1750°F environment.

3.1.2 Heat Exchanger

Using a mixture of $2\text{H}_2:\text{CO}_2$ gas and an electrical heater to simulate the reactor, the heat exchanger was tested for pressure drop at rated flow and for outlet temperature on the cold side. The first heat exchanger, four feet in length, had a pressure drop of 0.13 psi and an outlet temperature of 280°F when equilibrium was reached. This heat exchanger had an effectiveness of 83.5%. Since this performance was not satisfactory, a new heat exchanger was designed, fabricated, and tested. With this six foot long heat exchanger, a pressure drop of 0.18 psi was measured along with the following temperatures:

1. Hot side inlet - 1220°F
2. Cold side outlet - 144°F
3. Cold side inlet - 92°F

Heat exchanger effectiveness was calculated to be 95%. This performance was deemed to be satisfactory. However, this same performance could not be expected during unit operation since the hot reactor is to be mounted inside the heat exchanger, thus causing performance degradation. Under these conditions, the cold side outlet temperature proved to be 260°F to 325°F.

3.1.3 Compressor

A simple flow rate versus output pressure test was performed on the compressor assembly. The rated output of the carbon-vane compressor was 1.0 CFM, running open, to 0.8 CFM at 10 psig outlet pressure. Due to faulty manufacture of the carbon vane compressor, only 40% of this performance was attained. Modification of the

carbon vane compressor in our shops increased the performance to 60% of rated output. A carbon vane compressor and motor were obtained and fabricated into a modified compressor. Full output was obtained with this compressor assembly. While operating with 60°F inlet gas temperature, an outlet gas temperature of 120°F is obtained. No leakage of reaction gases are observed from the compressor assembly.

3.1.4 Electrolysis Unit

The multiple-cell unit was placed in a test rig which included a means of feeding electrolyte and taking the gases off through a bubble trap. After purging with argon, the unit was filled with 110 ml of 6N KOH, 6 ml less than the calculated amount. This was done 1.5 hours before the power was turned on; however, this proved to be too short a time for proper soaking of the cells. The initial soaking of the unit is important for proper operation, since an incomplete wetting will make the cell act as if it were dehydrated. This, in fact, did happen and a small internal explosion was heard after the unit had been operating for five minutes at 10 amperes. A check made on a spare wick revealed that the heating necessary to cure the epoxy adhesions was sufficient to grossly alter the initial wicking properties of the polypropylene. As a result, the initial wetting was several times slower than might be expected. To insure complete wetting, the cell was then partially flooded. The excess electrolyte came over in the gas stream and the unit then operated well with no further electrolyte carry over. Table I gives some of the operating data obtained for the unit during various runs.

A run was made without adding feed water. When the unit was dehydrated, traces of hydrogen came over in the oxygen stream. When enough make-up water had been added, hydrogen was no longer detected. A properly hydrated cell does not allow hydrogen to come over the the oxygen side.

As the data show, the cell temperature seems to reach an equilibrium at about 125-130°F external temperature. A theoretical analysis shows that the bulk of the cell unit cooling is obtained by evaporative water losses during electrolysis. This water must be taken into account when calculating water consumption.

Figure 3-2 presents a curve giving the electrolysis unit voltage as a function of current density, as obtained from experimental data.

TABLE I
ELECTROLYSIS UNIT OPERATION

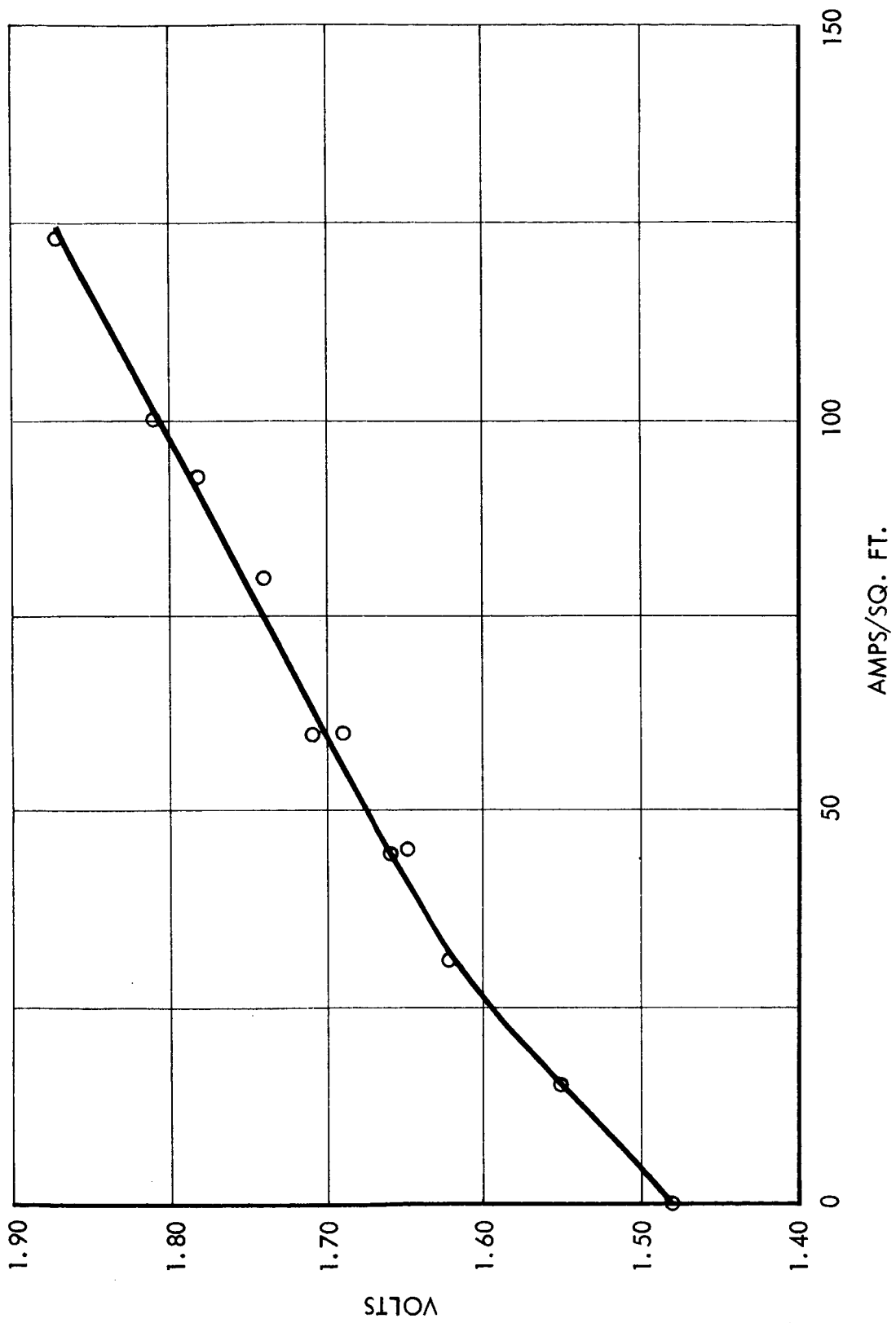
<u>Date</u>	<u>Operating Time</u>	<u>Cell Current</u>	<u>Average Voltage</u>	<u>Max. Cell Temp.</u>
9-29-63	1.5 hr	50 amps	1.60	100°F
9-30-63	4.0 hr	50 amps	1.60	125°F
11-13-63	6.5 hr	65 amps	1.80	124°F
11-14-63	2.25 hr	65 amps	1.85	125°F
11-14-63	3.50 hr	65 amps	1.80	126°F
11-15-63	2.75 hr	65 amps	1.80	133°F
11-15-63	6.00 hr	65 amps	1.80	133°F

Total Operating Time = 26.5 hours

65 amps = 100 amps/sq ft

3.2 Unit Tests

Prior to endurance runs, preliminary tests were being carried out to determine the true operating characteristics of the unit. It was planned to determine the reaction rates obtainable as a function of reactor temperature, condenser-separator temperature, and recycle gas flow rate. During this preliminary testing phase, the electrolysis unit was operated as a separate unit. The basic CO₂ reduction unit used in the testing is



H₂O ELECTROLYSIS UNIT - VOLTAGE VS. CURRENT DENSITY
 EXPERIMENTAL DATA (CELL TEMPERATURE = 125°F)

FIGURE 3-2

shown in Figures 3-3 through 3-7. Five views are shown of the unit just after completion of pressure checks prior to application of thermal insulation around reactor, heat exchanger, and filter assembly. Changes made in the unit since these photos were made are discussed in this report.

3.2.1 Experimental Run #1

Total running time was 130 minutes at an average reactor temperature of 1140°F, a condenser temperature of 70°F, and a reaction rate varying between 300-750 cc/min. The carbon blow-out cycle was tested, resulting in pressure build-up in the reactor and pressure decrease in the condenser-separator. Reaction water from the H₂O accumulator was drawn through the condenser-separator into the blower, causing complete system malfunction. The cause of the reactor blockage was not known. Unit overhaul commenced immediately.

3.2.2 Experimental Run #2

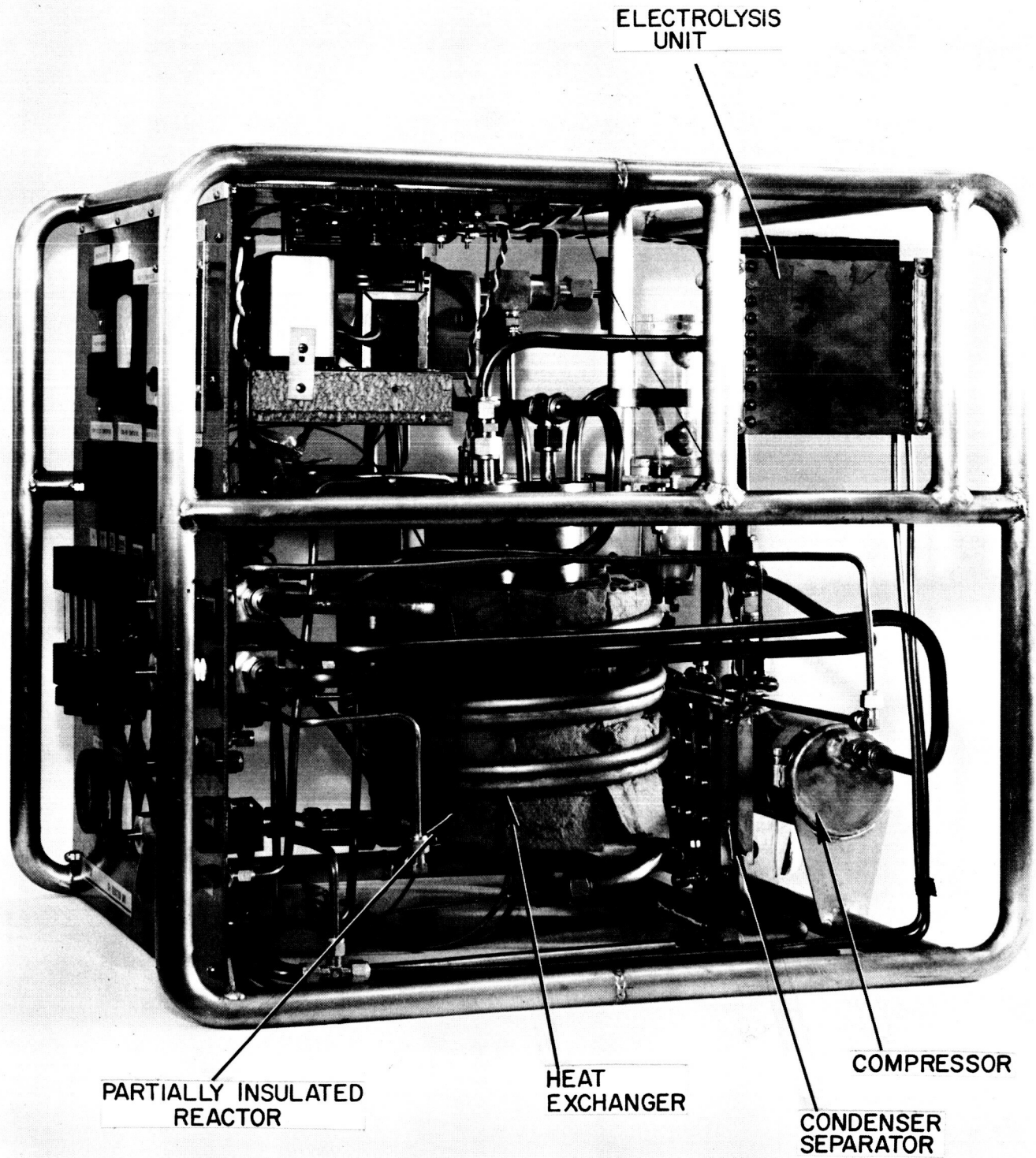
A summary of results of experimental run #2 is given in Table II. This run was terminated after 27 hours 10 minutes running time to make changes in the unit as dictated by experimental observation. These changes were:

1. Replace compressor with modified compressor design.
2. Replace plastic filter prior to condenser-separator with all metal filter housing.
3. Install moisture trap in recycle flow line after condenser-separator.
4. Install new columns in gas chromatograph and recalibrate.
5. Change piping arrangement for carbon blow out cycle.
6. Install shut-off valve between water reservoir and condenser-separator.

During run #2, the cause of the reactor blockage was determined as reaction water in the hot reaction gases condensing on the surface of the cold filter being switched into the cycle. The condensing water clogged the filter pores. This may be avoided by

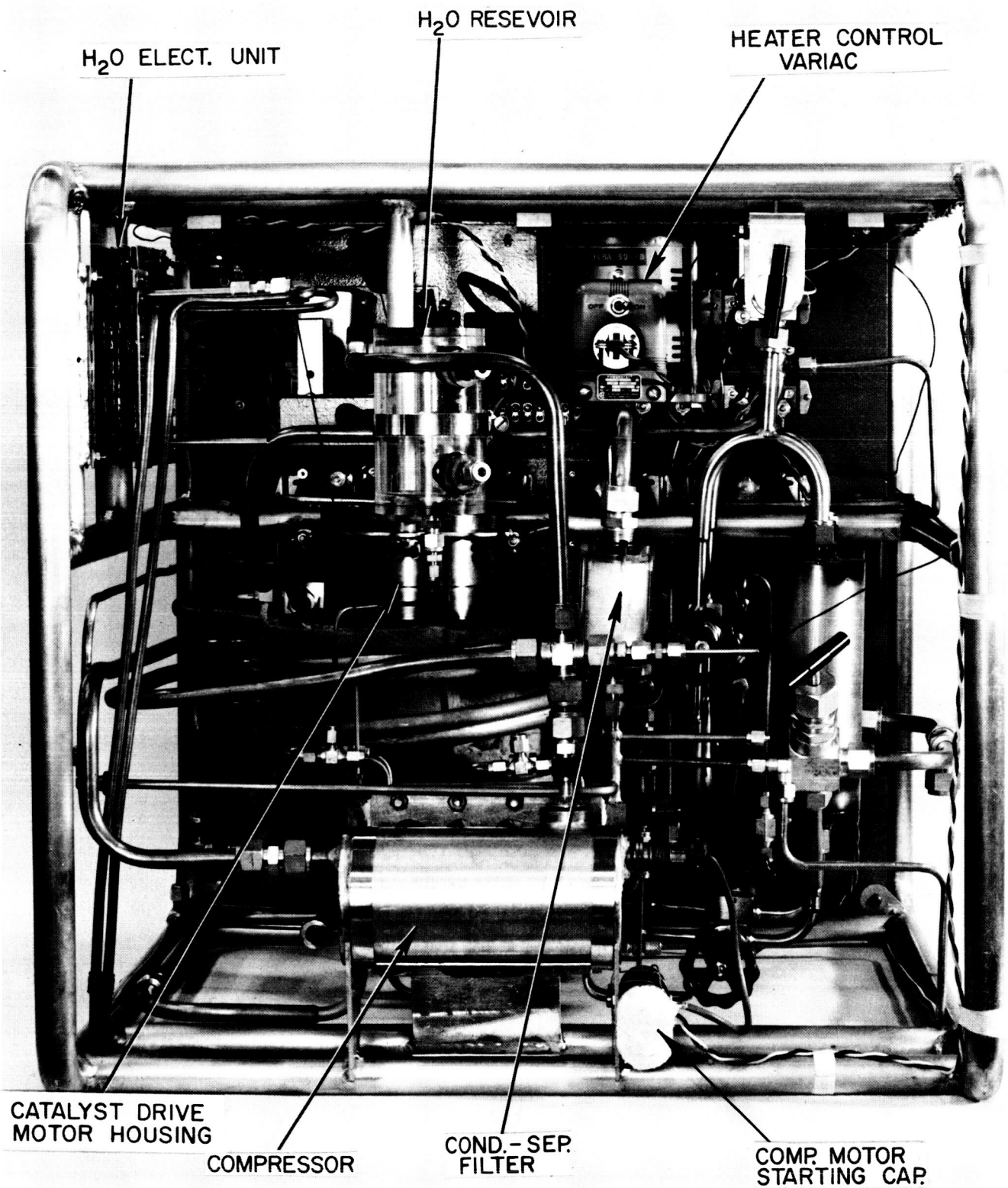


CO₂ REDUCTION UNIT - INSTRUMENT AND CONTROL PANEL



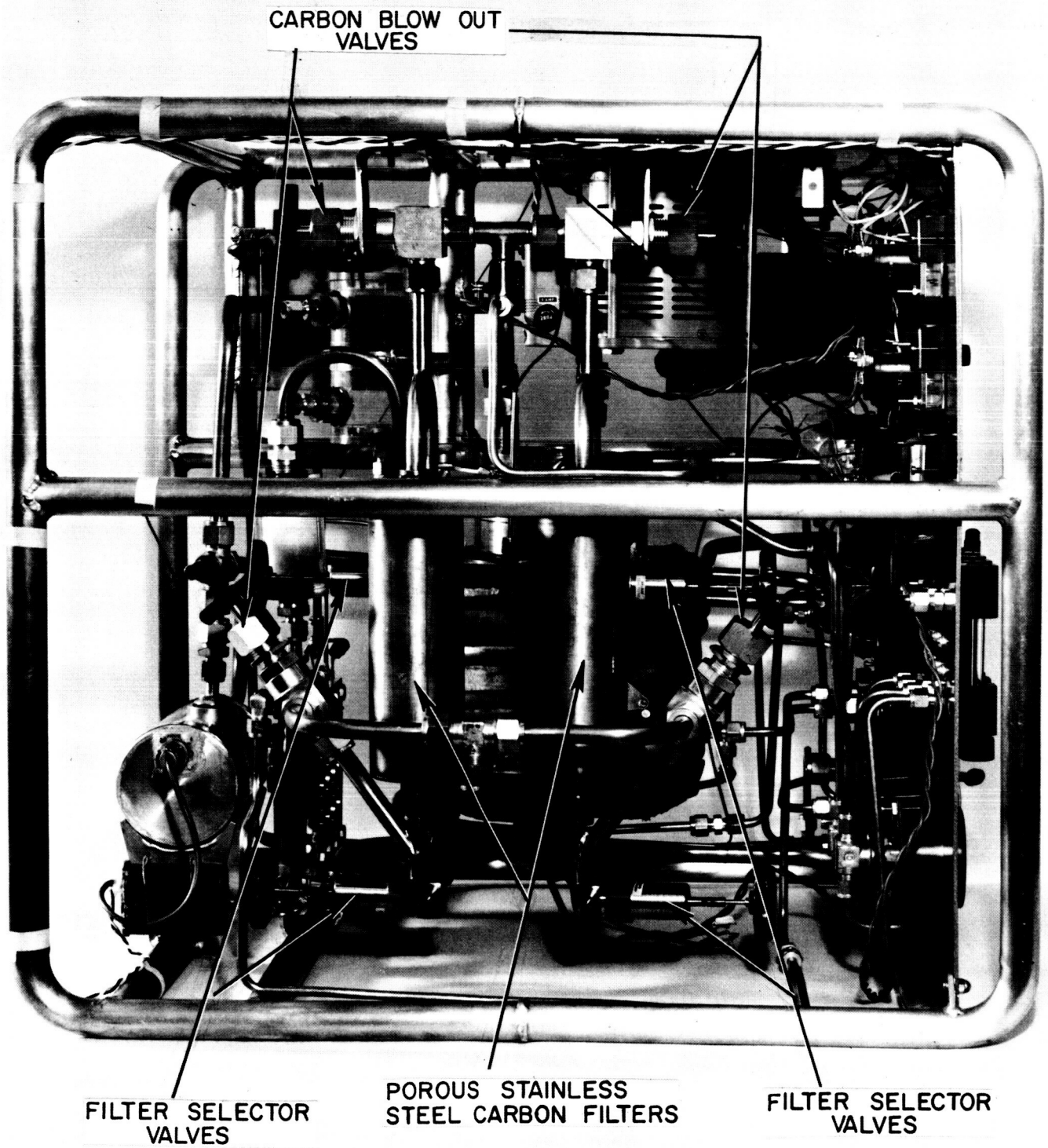
CO₂ REDUCTION UNIT - PARTIALLY ASSEMBLED

FIGURE 3-4



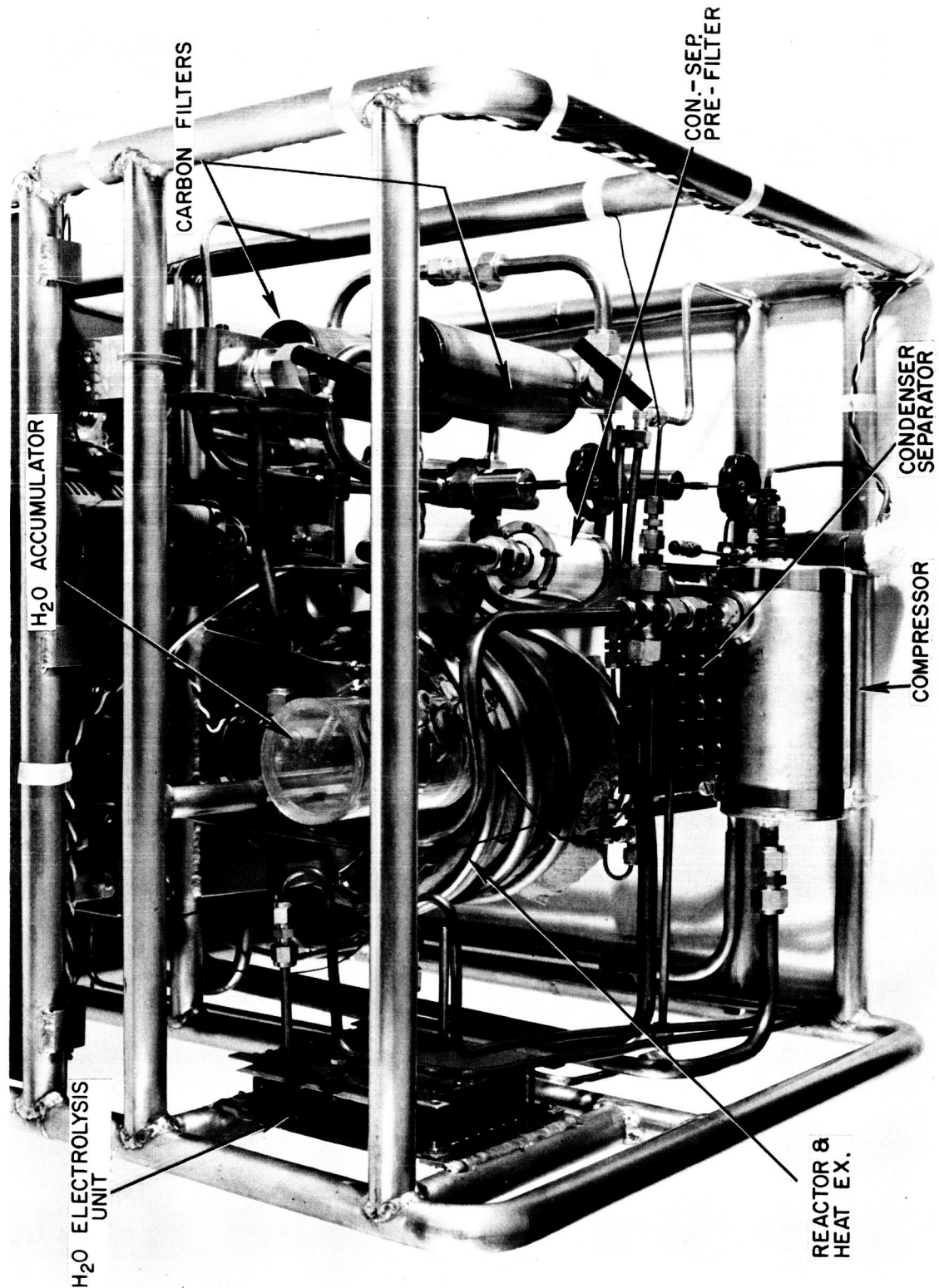
CO₂ REDUCTION UNIT - REAR VIEW

FIGURE 3-5



CO₂ REDUCTION UNIT - SIDE VIEW

FIGURE 3-6



CO₂ REDUCTION UNIT - TOP VIEW

FIGURE 3-7

TABLE II

EXPERIMENTAL RESULTS - RUN #2

Reactor Pressure = 2.0 psi Condenser Temp (Average) = 57°F

Date	Time	Feed rate cc/min	Recycle Flow Rate liters/min	Reactor Temp. °F	Heater Power Watts	Remarks
11-14-63	1030	-	-	1130	250	Begin feeding 2H ₂ :CO ₂ Gas Mixture
"	1115	490	15.5	1180	173	Additional H ₂ Feed
"	1200	343	-	1095	173	Water in Recycle Rotameter
"	1400	186	16.3	1080	211	Reaction Gas Comp. out of Balance
"	1445	320	16.3	1145	226	
"	1500	451	16.3	1150	214	
"	1615	183	15.0	1130	196	
"	1645	366	16.8	1125	196	
"	1815	329	13.8	1280	289	
"	1915	400	14.6	1335	64	
"	2030	246	16.3	1180	245	
"	2200	350	14.6	1240	231	
"	2400	285	12.4	1230	231	Attempt to Switch Filters
11-15-63	0050	328	16.3	1220	250	
"	0145	441	14.6	1240	260	
"	0330	391	16.3	1220	308	
"	0415	405	18.8	1240	292	
"	0500	336	20.0	1240	308	
"	0635	398	18.0	1240	292	
"	0715	323	20.0	1245	292	
"	0830	308	19.0	1255	292	68 cc/min H ₂ Feed
"	0930	416	19.0	1260	292	
"	1030	408	18.0	1260	292	
"	1130	422	18.0	1265	292	Gas Analysis - 1135 H ₂ - 13.8%, N ₂ -10.6%, CH ₄ - 24.1%, CO-39.5%, CO ₂ - 12.0%
"	1200	440	18.0	1265	292	CH ₄ -35.5%, CO-21.5%, CO ₂ -18.5% H ₂ -14.6%, N ₂ -11.5%
"	1230	421	21.5	1265	292	
"	1300	384	18.0	1265	-	Heater Off - Prepare for Shutdown
"	1317	428	16.3	1070	-	
"	1325	381	18.0	970	-	
"	1332	250	18.0	910	-	
"	1340	198	18.0	845	-	

preheating both filters when the unit is first started. Thermal insulation will prevent filters from cooling to a temperature low enough to cause condensation.

The erratic reaction rate was the result of unsatisfactory gas analysis being obtained with the chromatograph. Thus the recycle gas composition varied over a wide range, giving rise to the varying reaction rate.

After the entire unit had cooled and flow through both filters was again possible, the carbon blow-out cycle was operated successfully, depositing carbon in the carbon collector.

3.2.3 Experimental Run #3 Through #9

A series of short term experiments were carried out to obtain operating characteristics of the unit. In runs 3-6 both feed gases were fed from a bottle of $\text{CO}_2\text{-H}_2$ mixture. The $\text{CO}_2\text{-H}_2$ mixture was not exact (CO_2 rich) making it difficult to control the H/O in the recycle gas stream. Analysis by gas chromatograph was slow so that precise control of the gas composition was not possible. The carbon blow-out cycle was not activated since one filter inlet valve was clogged preventing filter changeover. It is believed that this clogging was a result of earlier malfunctions (water drawn into system through condenser). A steady reaction rate of approximately 700 cc/min was maintained for five hours during Run #6 with no manual adjustments required to maintain this rate. After completion of Run #6 the unit was disassembled to repair the reduction reactor (weld crack) and to clean out carbon formations built up during early runs. Additionally, all water passages required cleaning since a highly acidic product water was obtained ($\text{pH} \sim 1.0$). An analysis of the water was not made but water color indicated the presence of nickel ions. It is suspected that the acid formation was due to the decomposition of Freon gas used for leak checking which was not completely flushed out of the unit prior to operation.

Beginning with run #7 feed gas to the reduction unit was set-up to simulate the feed of H_2 from the electrolysis unit. H_2 and CO_2 were fed into the unit from separate bottles and the feed pressures and flows were individually adjusted. Control of flow rates was obtained by observation of panel flowmeters and adjustment of the blower by-pass valve to change the pressure differential between the H_2 and CO_2 feed inlet.

Run #8 was terminated shortly after start-up since the condenser-separator was not able to keep reaction gases from passing through the porous plates. It was at this point that the asbestos and stainless steel plates were replaced with nickel plates. Satisfactory sealing was obtained with the nickel plates.

The electrolysis unit was integrated with the reduction unit prior to the start of run #9. Proper operation of the electrolysis unit was achieved but the test was terminated when both carbon filter selector valves became clogged with carbon. At this point the entire unit was disassembled and cleaned. The high temperature globe-type valves were replaced with the TRW developed high temperature carbon plug valves.

Table III gives a summary of experimental runs 3 through 9. The values given in the table are representative of the stable portion of the respective experimental runs.

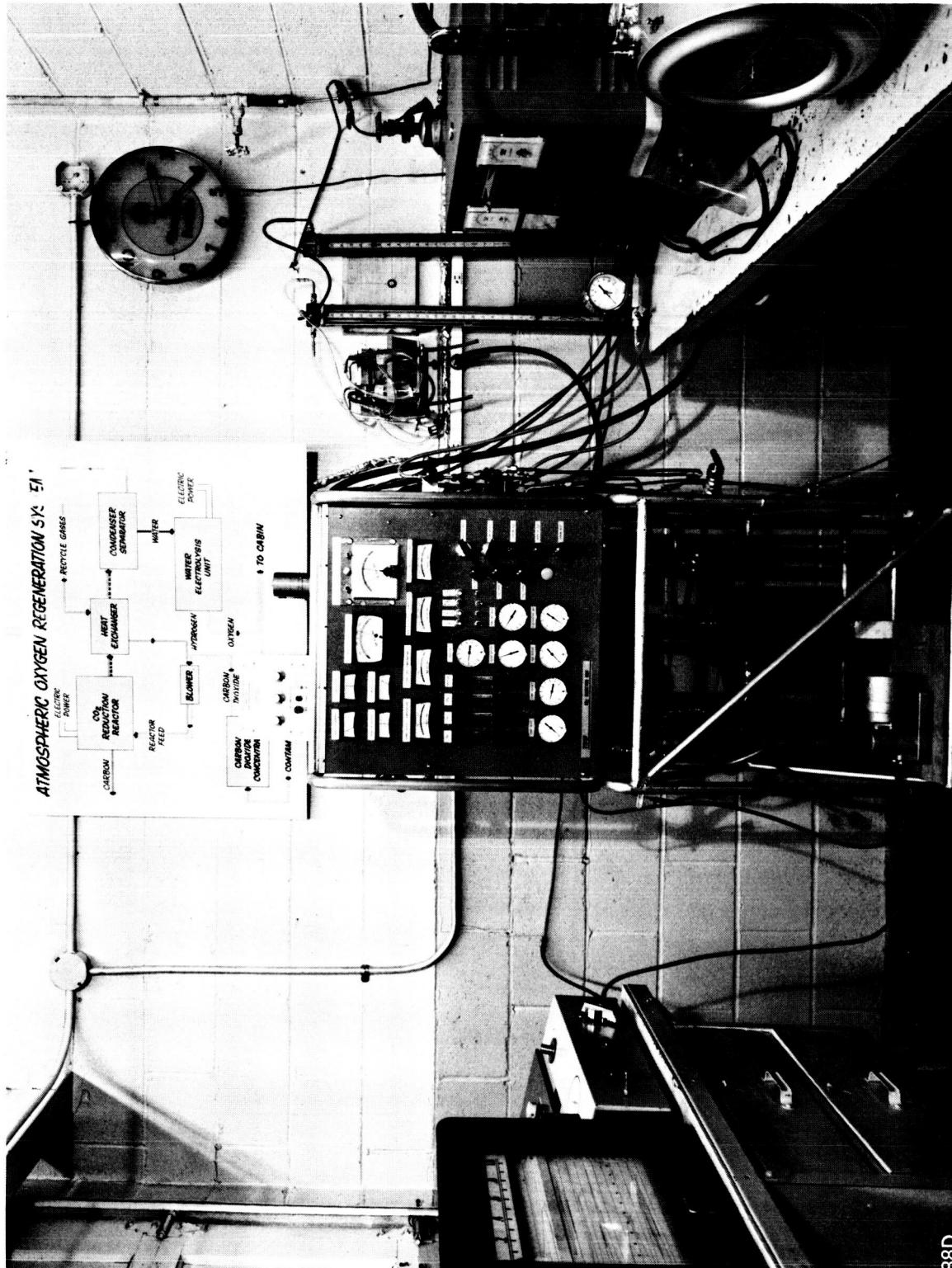
3.2.4 Experimental Run #10

Experimental run #10 was planned to be the first endurance run for the entire integrated CO_2 Reduction Unit. Figure 3-8 is a photograph of the experimental set-up used for the endurance testing program. Figure 3-9 is a close-up view of the low temperature carbon collector after the first transfer of carbon from the filters to the collector. Satisfactory performance of the unit with the electrolysis unit incorporated was observed for three hours. It was evident that the product water from the condenser-separator was causing performance degradation of the electrolysis unit. Because of this degradation it was decided to provide H_2 feed into the unit from a bottled source for the remainder of the run. Ion exchange resin beds would be added for water processing

TABLE III
EXPERIMENTAL RESULTS - RUNS 3-9

Run No.	Average Reaction Rate	Reactor Temperature	Condenser Temperature	Recycle Rate	Reactor Power	Running Time
3	742 cc/min	1090°F	62°F	21.2 L/min	228 watts	4 hr-45 min
4	652 cc/min	1100°F	53°F	21.0 L/min	245 watts	7 hr-10 min
5	793 cc/min	1200°F	59°F	19.0 L/min	265 watts	7 hr
6	689 cc/min	1210°F	60°F	17.4 L/min	268 watts	7 hr
7	766 cc/min	1000°F	53°F	19.0 L/min	290 watts	4 hr-45 min
8	NO DATA - Defective Condenser-Separator					
9	NO DATA - Carbon Filter Selector Valves Clogged					

Electrolysis Unit Operated Properly.



CO₂ REDUCTION UNIT ON TEST STAND

FIGURE 3-8



LOW TEMPERATURE CARBON COLLECTOR AFTER
FIRST FILTER BLOWBACK CYCLE

FIGURE 3-9

prior to the start of the next run. Run #10 was terminated when it became evident that carbon was building up in various flow lines as evidenced by the decreasing recycle flow rates. The unit was modified to prevent this carbon build-up during future testing. Figure 3-10 presents a plot of reaction rate, reactor temperature, condenser temperature and recycle flow rate as a function of running time after heater start-up. Insufficient gas analyses were performed to correlate reaction rate with recycle gas composition.

3.2.5 Experimental Run #11

Run #11 was planned as an endurance run with the electrolysis unit operating in conjunction with the reduction unit. Product water from the reduction process was filtered through an ion exchange bed before being metered into the electrolysis unit. The electrolysis unit supplied hydrogen to the reduction unit for seven hours, at which time a crack developed in an epoxy bond between a plastic and metal part of one cell. The reduction unit operated for a total of 76.5 hours before termination of the run due to degradation of the lower catalyst shaft bearing. During the active running time the average reaction rate was maintained above the design rate of 600 cc/min. Table IV presents a typical set of data obtained during the run.

3.2.6 Experimental Run #12

For run #12 the reduction unit was operated without an electrolysis unit (a new electrolysis unit was under fabrication). Total operating time for this run was 9 days. At some point in the run (estimated to be 2 days after start) the drive shaft from the drive motor became worn to the point that catalyst rotation stopped. Operation of the unit continued without carbon removal from the reactor. The reaction rate remained high until the carbon filled all voids in the reactor vessel at which time a significant decrease in reaction rate was observed. Carbon removed from the reactor after this run was caked into a relatively hard deposit. Table V presents a summary of the results obtained in Run #12.

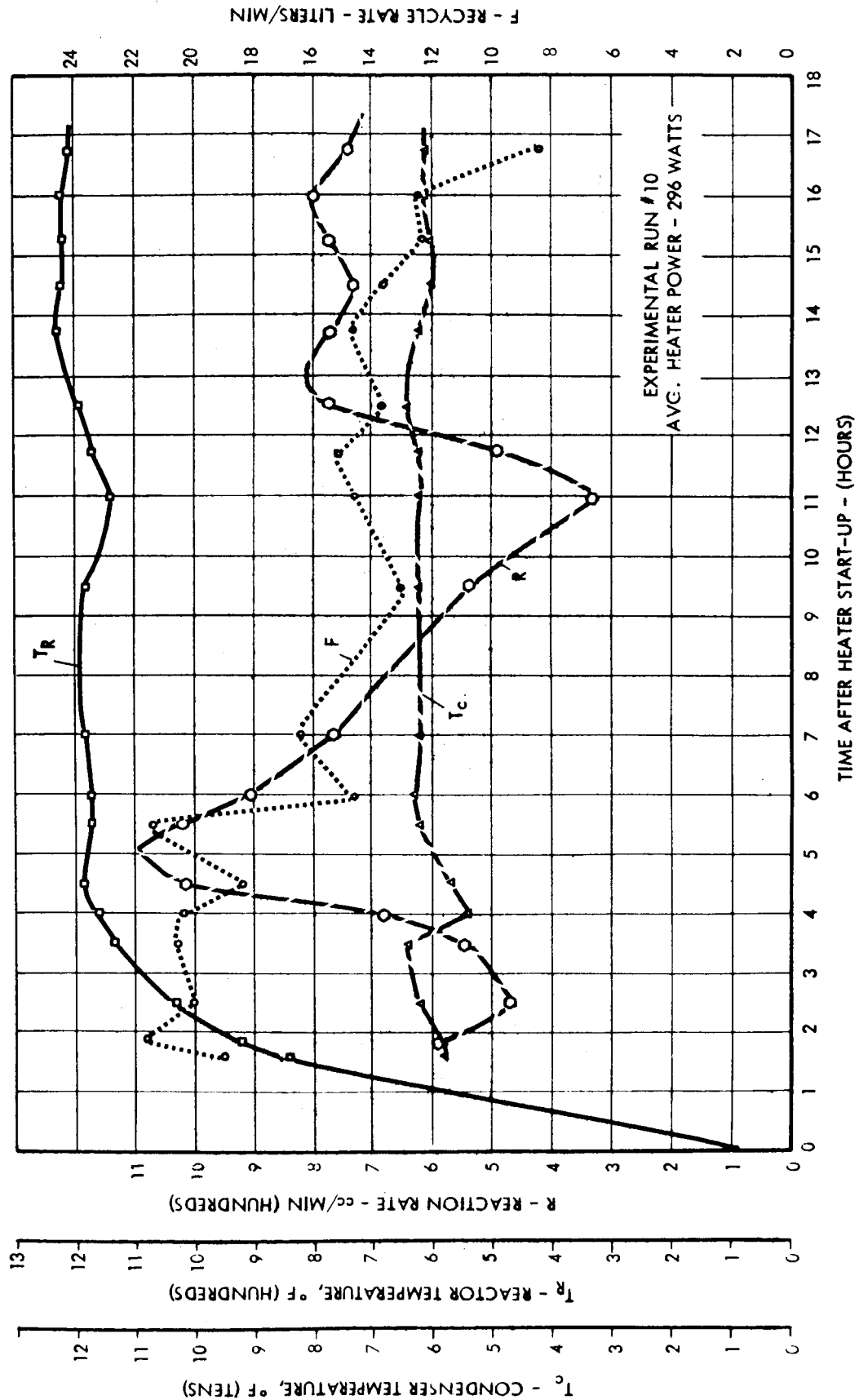


FIGURE 3-10

TABLE IV
EXPERIMENTAL RUN #11-26 HOURS AFTER START-UP

Total CO ₂ Feed	375 liters
Instantaneous Reaction Rate	738 cc/min (wet test meter)
Recycle Flow Rate	16.4 liters/min
Reactor Temperature	1180°F
Condenser Temperature	59°F
Compressor Outlet Temperature	105°F
Heat Exchanger Outlet Temperature	290°F
Reactor Inlet Temperature	520°F
Reactor Pressure	2.0 psig
Filter Outlet Pressure	1.25 psig
Condenser-Separator Inlet Pressure	1.15 psig
Compressor Inlet Pressure	15 in. H ₂ O
Compressor Outlet Pressure	2.1 psig
Condenser-Separator H ₂ O Outlet Pressure	20 in. H ₂ O
Electrolysis Unit H ₂ Outlet Pressure	26.5 in. H ₂ O
Reactor Heater Current	2.9 amps
Reactor Heater Voltage	116 volts
Compressor Current	0.96 amps
Compressor Voltage	112 volts
CO ₂ Flow Rate	200 cc/min (rotameter reading)
H ₂ Flow Rate	375 cc/min (rotameter reading)
O ₂ Flow Rate	200 cc/min (rotameter reading)
Catalyst Drive Motor Current	28.5 ma
Electrolysis Unit Current	55 amps (85 amps/ft ²)
Electrolysis Unit Voltage	1.68 volts
Electrolysis Unit Temperature	106°F
Gas Analysis	
Volume % H ₂	46.0%
Volume % N ₂	4.4%
Volume % CH ₄	29.0%
Volume % CO	10.5%
Volume % CO ₂	10.1%
H/O - Hydrogen Oxygen Atom Ratio	6.8

TABLE V
EXPERIMENTAL RUN #12

Date	Time	Reaction Rate, cc/min	Reactor Temperature, °F	Condenser Temperature, °F	Recycle Rate Liters/min.	H/O
2-25-64	1830	642	1105	80	15	
2-26-64	0600	300	1110	61	16.4	60.4
	1830	552	1110	67	19.8	3.1
2-27-64	0630	414	1095	71	20.2	19.6
	1830	636	1120	62	20.5	8.3
2-28-64	0630	558	1120	55	20.5	3.9
	1830	540	1120	63	19.8	2.9
2-29-64	0630	570	1110	59	20.5	5.2
	1830	546	1120	60	18.6	7.3
3-1-64	0530	723	1140	57	18.0	6.61
	1740	699	1150	64	18.0	11.2
3-2-64	0630	579	1135	61	19.0	11.3
	1620	675	1150	61	18.4	8.0
3-3-64	0630	645	1170	73	18.0	2.1
	1615	615	1180	72	18.0	6.5
3-4-64	0830	489	1165	68	16.0	1.33
	1820	498	1185	66	18.8	4.03
3-5-64	0630	375	1170	65	18.8	8.9
	1530	324	1190	62	18.0	-

3.3 Endurance Run - Experimental Run #13

A successful run of 25 days continuous operation was accomplished by run #13. Operation of the unit ceased on contract termination date with full operational capability. For this run the catalyst drive was modified such that the plates were cleaned every 24 hours by manual activation. In this mode of operation carbon was successfully removed from the unit for the entire 25-day operation. The new electrolysis unit was successfully operated with the reduction unit during this run, but not for the entire 25-day test. Without automatic controls on the unit it is not possible to maintain a balanced H_2 output and reduction unit reaction rate. Establishing a balanced operation of the reduction unit and electrolysis unit does not appear to be especially difficult. Table VI presents a summary of the 25-day endurance run.

Typical Operation of Electrolysis Unit in Rig

Electrolysis Unit Current	-	58 amps
Electrolysis Unit Voltage	-	1.84 volts
Electrolysis Unit Temperature	-	115°F
Hydrogen Flow Rate (Rotameter)	-	410 cc/min
Oxygen Flow Rate (Rotameter)	-	205 cc/min

As an individual unit the electrolysis cell was operated for a total of 15 days on one continuous run. The average unit current maintained was 30 amps at a cell voltage of 1.90 volts. For these conditions the cell temperature was 115°F. Performance degradation was observed since the feed water was not passed through ion exchange beds (laboratory water is slightly acidic and electrolyte is a base).

3.4 Analysis of Products

Characteristics of the various products of the reduction unit which were easily attainable are tabulated as follows:

TABLE VI
EXPERIMENTAL RUN #13

Date	Time	Reaction Rate, cc/min	Reactor Temperature, °F	Condenser Temperature, °F	Recycle Rate Liters/min.	H/O
3-8-64	1710	660	1105	56	15.3	
3-9-64	0630	606	1135	68	15.5	
3-10-64	0330	690	1170	77	15.5	8.1
	1630	670	1180	78	15.2	
3-11-64	1640	771	1170	77	18.0	
3-12-64	1805	810	1180	79	16.4	5.6
3-13-64	1630	600	1160	79	18.0	
3-14-64	1730	480	1175	77	17.0	12.0
3-16-64	0625	630	1170	78	17.4	
	1700	610	1200	84	14.5	21
3-17-64	1430	710	1210	78	18.0	
3-18-64	1710	560	1200	79	17.0	
3-19-64	1710	570	1195	84	17.0	
3-20-64	1600	540	1200	68	14.5	
3-21-64	1000	480	1180	72	13.0	
3-22-64	2200	480	1200	75	9.8	
3-23-64	1715	565	1240	56	13.6	
3-24-64	0750	900	1280	51	9.8	
3-25-64	0757	540	1270	57	9.2	
3-26-64	1945	795	1220	57	11.5	
3-27-64	1635	540	1240	56	11.4	
3-30-64	0845	790	1080	57	16.4	
3-31-64	1700	600	1185	54	14.5	
4-1-64	1720	375	1250	59	14.5	
4-2-64	1600	260	1210	57	11.2	

3.4.1 Carbon

Density in Carbon Collector	0.40 gm/cc	
Density After Compression	0.67 gm/cc	
Particle Size	20% 44 μ , Bulk - 44-74 μ	
Magnetic Properties	Slightly Magnetic	
Iron Content by Weight Percent and Run No. of Sample	% Fe	Exp't Run No.
	10.9%	Preliminary TRW Test
	20.51%	#2-6
	15.44%	#10
	11.90%	#11
	16.85%	#13
Iron Compound Present	Fe_3C	
Form of Carbon	Largely Graphite	
Specific Surface Area	118 M^2/gm - Preliminary TRW Test	
	138.6 M^2/gm - Run #13	

3.4.2 Water from Condenser-Separator

Run #11		
Impurities in Solution	Trace of	Co, Pb & Sn
	Minor Impurities	Al, Ca, Cr, Mo, Mn & Zn
	Appreciable Impurities	B, Cu, Fe, Mg, Na, Ni, K & Si
Odor	Very Slight Organic	
Taste	Pronounced Organic	
Color	Satisfactory	
Appearance	Clear, No Sediment, Some Very Fine Suspended Particles	

Conductivity	64 Micromhos/cm
pH	7.3
Solids	Average 113 ppm

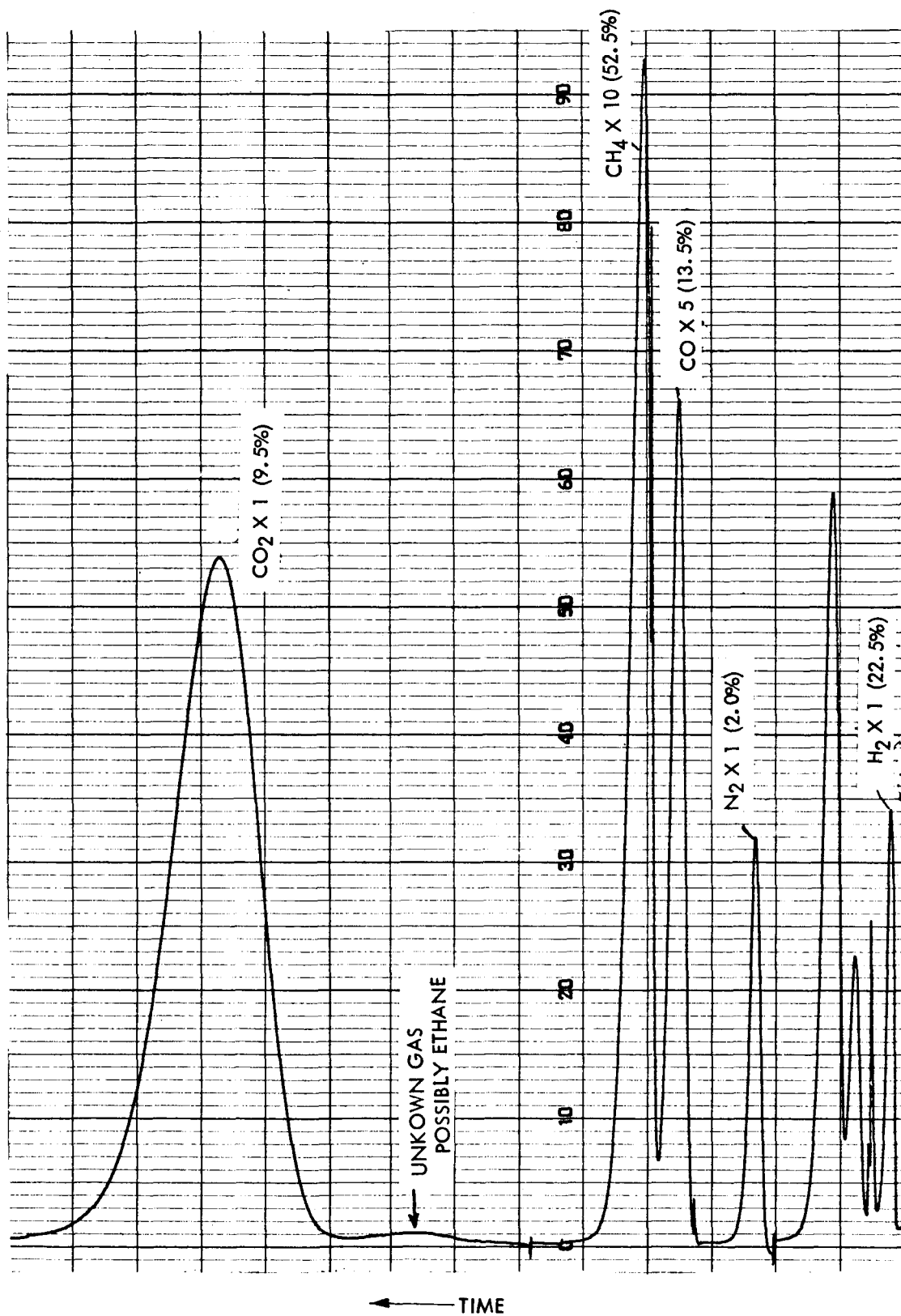
Water from Run #13 was not tested but was much clearer and had less color than tested sample.

3.4.3 Recycle Gas Analysis

The recycle gas analysis varies continuously as the CO_2 - H_2 feed ratio changes. A typical analysis by gas chromatograph is shown in Figure 3-11. Note the very slight peak just prior to the CO_2 peak. This peak is not normally present until the unit is run for very long periods (days) with no gas bleed out of the system. The unknown gas may be ethane building up to a detectable concentration.

3.4.4 Electrolysis Unit Output Gases

A chromatographic analysis of the O_2 and H_2 gas from the electrolysis unit was not performed. However, when H_2 from the unit was fed into the reduction reactor no previously unobserved gases were detected by gas chromatography.



RECYCLE GAS CHROMATOGRAM

FIGURE 3-11

4.0 RECOMMENDATIONS

Based on experimental results obtained with the present unit the following program is recommended.

1. The present unit should be equipped with automatic controls to maintain a steady reaction rate with unattended operation.
2. Carbon flow lines in the present unit should be modified to permit automatic carbon blow out.
3. The improved unit should be used as an investigative tool to gain more insight into the reduction of CO_2 by hydrogen with various catalyst materials under varying reaction conditions. This information is needed to design a reduction reactor having extremely low or no catalyst consumption.
4. As a means of increasing the reaction rate obtainable with given reaction conditions the use of a regenerable chemical recycle gas dryer should be investigated. Figure 4-1 presents a schematic of this proposed addition to the system. A dryer such as this is capable of doubling the reaction rate for given conditions. This leads to lower total electrical power consumption and smaller unit volumes.
5. An electrolysis unit should be constructed using a gasket-type of construction rather than epoxy bonding of cell pieces.
6. An electrochemical CO_2 concentration (TRW Carbonation Cell) unit should be built and integrated with the improved unit.

**SCHEMATIC REPRESENTATION OF CO₂ REDUCTION SYSTEM USING
REGENERATIVE CHEMICAL DRIERS FOR REMOVAL OF REACTION WATER**

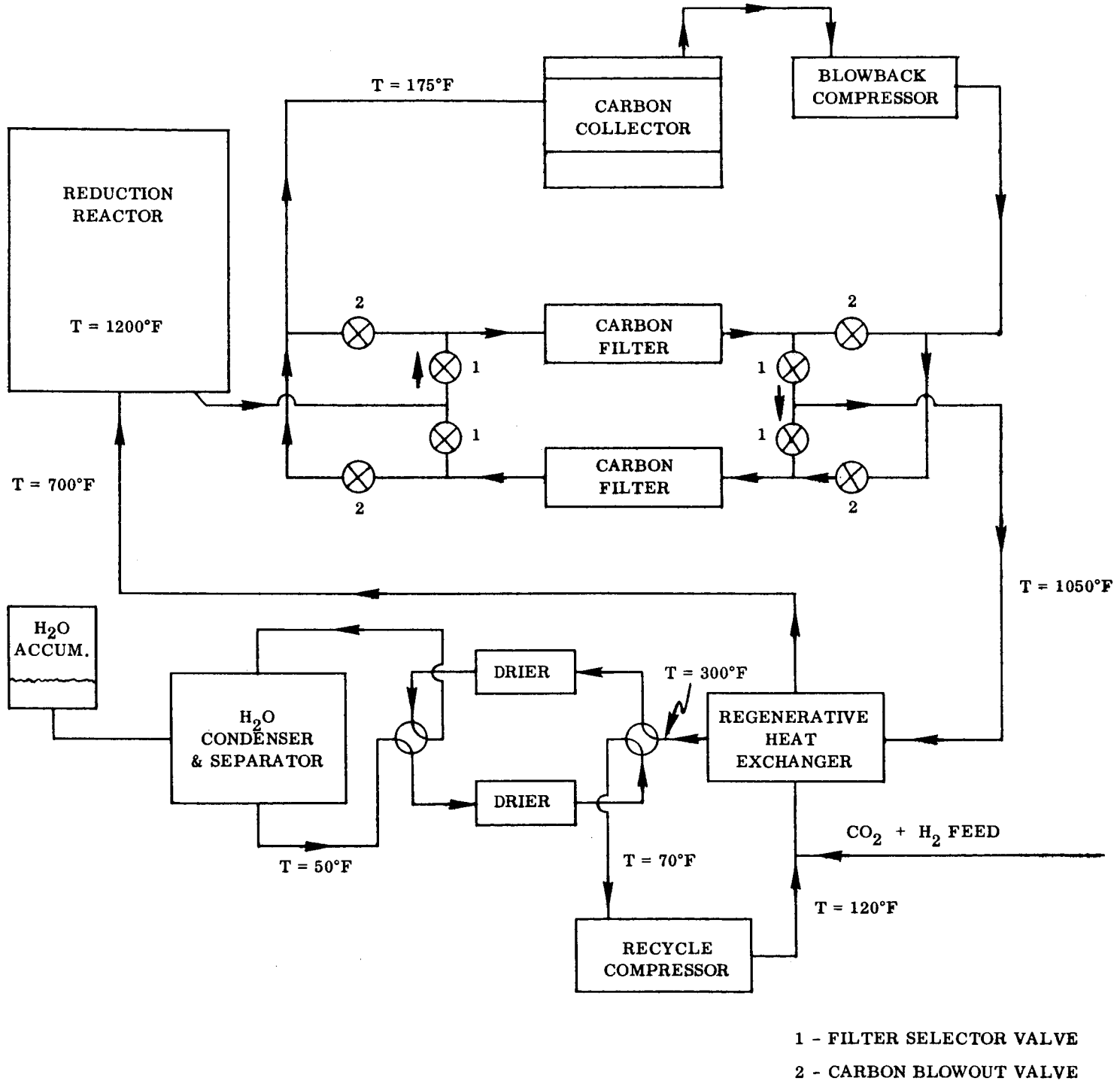


FIGURE 4-1

7. The new integrated oxygen regeneration system should be tested in a closed cabin to determine what, if any, toxic gases may be produced. There is the possibility that the TRW CO₂ Reduction Reactor could process gases normally considered toxic.
8. Investigate the use of the carbon produced by the reduction process for an odor control agent in a closed cabin.

5.0 CONCLUSIONS

On the basis of experimental results obtained, the following conclusions are believed to be justified.

1. Construction of reactors using flat iron plates as catalyst is entirely feasible.
2. Continuous carbon removal from the reactor is possible and practical.
3. Porous stainless steel filters can be cleaned and used continuously.
4. Reaction water can be successfully removed by a completely static device.
5. Extremely compact and efficient water electrolysis units can be built.
6. Satisfactory reaction rates can be continuously maintained by proper control of feed gases.
7. CO_2 reduction by H_2 over iron catalyst appears to be feasible for adaptation to space requirements.
8. Catalyst consumption rates are low enough such that this system is competitive with other methods of CO_2 reduction.
9. The iron catalyst does not degrade with time and does not require regeneration by hydrogen.
10. Extremely smooth flow lines are required for carbon transport.
11. Additional experimentation should be carried out as stated in Section 4.0 - Recommendations.

REFERENCES

1. "Carbon Dioxide Reduction System, " TRW Report No. ER-4351, February 17, 1961.
2. "Electrolytic CO₂ Reduction System, " TRW Report No. ER-4701, December 15, 1961.
3. Foster, J. F., and J. S. McNutty, "Study of a Carbon Dioxide Reduction System, " ASD TR 61-388, August, 1961.
4. Remus, G. A., R. B. Neveril, and J. D. Zeff, "Carbon Dioxide Reduction System, " Report MR 1163-50, Contract No. AF 33(616)-8223, September, 1962.
5. "The Reduction of Carbon Dioxide Using a Fluidized Catalyst Bed, " TRW Report No. ER-5159, Contract No. Nonr 3431(00)(FBM), December 15, 1962.